



Preface to the Second Edition.

In this second edition of the New Intermediate Chemical Calculations, the authors have thoroughly revised the book, and made a number of improvements. The book has been divided into two parts :—

In part I are dealt calculations based on Physical and Inorganic Chemistry and in part II calculations based on Organic Chemistry.

A large number of exercises and University questions up-to-date have been added to the different chapters.

The original term cubic centimetre which has now been discarded (by the scientific world) is replaced by the new term milli litre.

It is hoped that Intermediate students will find this book to be very useful and helpful towards the thorough understanding of all types of Chemical Calculations.

Suggestions from fellow teachers are most welcome.

Authors

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ORGANIC

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NEW

INTERMEDIATE CHEMICAL CALCULATIONS

PART I INORGANIC

CHAPTER I

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UNITS OF MEASUREMENTS

There are two systems of units of measurements in use :—

- [i] The English System and
- [ii] The French System

The English System. This System is called Foot-Pound Second System or *F. P. S.* System. The units are:—

Length	12 inches	= 1 Foot
	3 Feet	= 1 Yard
	220 Yards	= 1 Furlong
	8 Fl. or 1760 yds.	= 1 Mile
Mass	16 Ounces	= 1 Pound lbs.
	28 Pounds	= 1 Quarter
	4 Quarters	= 1 Hundredweight Cwt.
	20 Cwts	= 1 Ton

These units are followed by the English only.

The International System of Units. The French System is called Centimetre=Gram=Second or *C. G. S.* System. It is very convenient and is adopted all over scientific world. It is, therefore, called the International System of units of measurements.

The chief advantage of this system is that the various divisions are multiples and submultiples of ten. Thus the fractions, one-tenth, one hundredth and one-thousandth part of the units are represented by attaching prefixes deci-, centi- and milli-respectively, while the prefixes deca-, hecto-, and kilo are used to represent ten, hundred and thousand times the unit respectively.

(i) **Length.** The unit of length used in the C. G. S. System is "Metre." It represents the length of the distance between two fine lines marked on a certain iridio-platinum standard bar at 4°C , kept at Paris. The submultiples of this unit are commonly used in the laboratory and mutiple parts of it for longer measurements.

They all are :—

Millimetre = $\cdot 001$ metre = $\cdot 03937$ inches.

10 Millimetres = 1 Centimetre = $\cdot 01$ Metre = $\cdot 3937$ inches.

10 Centimetres (cm) = 1 Decimetre = $\cdot 1$ Metre = $3\cdot 3937$ „

10 Decimetres = 1 Metre = $39\cdot 37$ Inches.

10 Metres = 1 Decametre = $393\cdot 7$ Inches.

10 Decametres = 1 Hectometre = $3937\cdot 0$ „

10 Hectometres = 1 Kilometre = $39370\cdot 0$ „

1000 Millimetres (mm.) = 100 Centimetres (cm.) = 10 Decimetres
= 1 Metre (m.)

1000 Metres (m.) = 100 Decametres = 10 Hectometres
= 1 Kilometre (km.)

Volume. The unit of volume commonly used in the Laboratory is the cubic centimetre (c. c.) or a millilitre (m. l.) as it is usually called these days. It represents the volume occupied by a cube whose edge is 1 cm. long. The bigger unit of volume is a cubic decimetre (called a litre) which is the volume occupied by a cube with an edge 1 decimetre in length.

Thus,

1000 Millilitres (cubic centimetres)	= 1 Litre
100 Centilitres	= 1 Litre
10 Decilitres	= 1 Litre
10 Litres	= 1 Decalitre
100 Litres	= 1 Hectolitre
1000 Litres	= 1 Kilolitre.
1 Litre	= 1.76 pints

A litre of water at the ordinary temperature, is equal to about $1\frac{1}{15}$ of the volume of one seer of water, and $1\frac{3}{4}$ pints.

[iii] **Mass.** The bigger unit of mass is called a **Kilogram** and is the mass of a platino-iridium block preserved in Paris. The smaller unit of mass is called a **gram** which is the mass of 1 mililitre (cubic centimetre) of pure water measured at 4°C .

The multiple and submultiple of gram units, therefore are :—

1000 Milligrams (mg.)	= 1 Gram. (gm.)
100 Centigrams (cg.)	= 1 Gram.
10 Decigrams	= 1 Gram.
10 Grams	= 1 Decagram
100 Grams	= 1 Hectogram
1000 Grams	= 1 Kilogram (Kg)
1 Gram	= 15.4323 Grains.

One Kilogram is equal to about 17.143 chhataks or 2.2 lbs.

EXAMPLE 1. *Sound travels 1130 ft. in a second. How many metres does it pass through per second?*

Velocity of sound in a second in feet = 1130 ft.

“ “ “ in inches = 1130×12 inc.

Since 39.37 inches = 1 metre,

\therefore Velocity of sound per second $\frac{1130 \times 12}{39.37} = 344.3$ metres.

EXAMPLE 2. *The diameter of a gas holder is 40 cms. and its height is 20 cms. Find the volume of coal gas in litres required to fill it.*

The capacity of the holder

= Height \times area of the base.

= Height $\times \pi R^2$ (where R is radius).

= $20 \times 3.1416 \times 20 \times 20$ m.l. (c.c.)

= 25132.8 m.l. (c.c.)

= $\frac{25132.8}{1000}$ (= 25.133) litres.

EXAMPLE 3. *Determine the mass in kilograms of pure water at 4° C. required to fill a tank 3 metres long, 2 metres wide and 125 cm. deep.*

Volume of tank = length \times breadth \times depth.

= $300 \times 200 \times 125$ m.l. (c.c.)

= 7500000 m.l. (c.c.)

But 1 m.l. of water at 4° C. weighs 1 gm.

\therefore 7500000 m.l. “ “ 7500000 gms.

= $\frac{7500000}{1000}$ = 7500 kilograms

Problems

1. One m.l. (c.c) of water at 15° C weighs .998 grams. Calculate the number of grams of water required to fill a vessel with a capacity of 30 litres.

2. The barometer reads at 29 inches, what will be its reading in millimetres?
3. Calculate the number of cubic inches in a litre and the number of litres in a cubic foot. A metre is equal to 39.37 inches.
4. How many grams of water will be required to fill a cylinder of 3 inches radius and 6 inches height?
5. The cylinder of a steam engine is 3 feet in diameter and 5 ft. long. How many cubic feet of steam at normal pressure will it contain?
6. The sun is at a distance of 92 million miles from earth. How many kilometres is it from the earth?
7. Light travels 186,000 miles per second. What is the speed of light in kilometres per sec.?

CHAPTER II

DENSITY AND SPECIFIC GRAVITY

The mass of unit volume of a substance is known as its **Density**. If M be the mass of volume V of a substance then the density D is calculated to be :—

$$D = \frac{M}{V}$$

This density is also called **Absolute Density** Or **Normal Density**. The units of mass and volume used must be mentioned in stating the density of a substance. Thus 1 m.l. (c.c.) of water at 4°C . weighs one gram, therefore density of water is 1 gram per m.l. (c.c.) at 4°C while 1 cubic foot of water weighs 62.5 lbs. at 4°C , therefore density is 62.5 lbs. per cubic foot. The density may, therefore, be expressed in either grams per m.l. (c.c.) or lbs. per cubic foot.

EXAMPLE 1. *A piece of metal occupies a volume of 6 m.l. (c.c.) and weighs 52.2 gms. Find its density.*

$$\text{Since } D = \frac{M}{V}$$

$$\therefore \text{ its density } = \frac{52.2}{6} = 8.7 \text{ gms. per m.l. (c.c.)}$$

EXAMPLE 2. *What is the volume occupied by 952 gms. of mercury when its density is 13.6 gms. per m.l.*

13.6 gms. of mercury occupy 1. m.l.

$$\therefore 952 \text{ gm mercury occupy } \frac{952}{13.6} = 70 \text{ m.l.}$$

Since the value of density varies with the system of units used to measure mass and volume, the confusion can be avoided if the relative densities of substances are referred to.

The Relative Density of a substance is the ratio of its density to that of the standard substance.

In the case of solids, liquids and solutions, the standard substance used is water at 4°C , and their relative density is termed **specific gravity**. The relative density of gases and vapours is called **Vapour Density**. **Hydrogen** is used as the standard substance in their case. Sometimes **Air** is used in place of hydrogen as the standard substance. In this case the vapour density of a substance determined with respect to hydrogen as the standard substance is to be multiplied by 14.4 in order to express it in terms of air as the standard substance.

$$\begin{aligned} \text{Relative density} &= \frac{\text{Density of the substance}}{\text{Density of the standard substance}} \\ &= \frac{\text{Wt. of a unit volume of the substance}}{\text{Wt. of the unit volume of the standard substance.}} \\ &= \frac{\text{Wt. of a vol. } V \text{ of the substance}}{\text{Wt. of the same vol. } V \text{ of the standard substance.}} \end{aligned}$$

$$\text{Thus Relative density (of solids and liquids)} = \frac{\text{Wt. of a vol. } V \text{ of the substance}}{\text{Wt. of same vol. } V \text{ of water,}}$$

Vapour Density (of gases and vapours.)

$$= \frac{\text{Wt. of a volume } V \text{ of a gas. or vapour at N. T. P.}}{\text{Wt. of the same volume } V \text{ of Hydrogen or air at N.T.P.}}$$

EXAMPLE 3. The weight of 25.0 m.l. of alcohol is found to be 19.88 gms. What is the specific gravity of alcohol?

25 m.l. of alcohol weighs 19.88 gms.

25 m.l. of water „ at 4°C . 25 gms.

$$\therefore \text{sp. gr. of alcohol} = \frac{19.88}{25} = .795.$$

EXAMPLE 4. Find the weight of 300 c. c. block of a metal of which the specific gravity is 8.5.

1 m.l. of the metal weighs 8.5 gms.

300 m.l. „ „ weigh $8.5 \times 300 = 2550$ gms.

EXAMPLE 5. What is the volume occupied by 144 gms. of HCl of specific gravity 1.2. ?

1.2 gms. of acid occupy a volume of 1 m.l.

144 „ „ „ a „ of $\frac{144}{1.2}$ ml. = 120 m.l.

NOTE. Sometimes the amount of a substance is expressed in percentage. In case of solids the % age refers to weights, in case of gases to volume and in case of liquids or solutions to weight or volume as may be evident from the context. Thus 20 percent sulphuric acid would mean 20 gms. of the acid in 100 m.l. of the acid solution and so on.

EXAMPLE 6. Find the weight of 20 percent solution of sodium carbonate of specific gravity 2.6 which should be evaporated to give 50 gms. of the solid.

20 gms. solid is present in the solution having a volume = 100 m.l. (c.c.)

\therefore 50 gms. solid can be obtained from solution having a volume = $\frac{50 \times 100}{20} = 250$ m.l.

\therefore sp. gr. of the solution = 2.6

\therefore weights of 250 m.l. of the solution = 250×2.6 gms.
= 650 gms.

Composition of mixtures— The composition of mixtures can be calculated from densities with the help

of the general formula. In this case it must be remembered that the total mass or volume of a mixture is always equal to the sum of masses or volumes of the components.

EXAMPLE 7. *A sample of air containing Oxygen and Nitrogen only has a density of 14.4 with respect to hydrogen. The densities of constituent gases are 16 and 14 respectively relative to hydrogen. Find the composition of the mixture by volume and by weight.*

(a) **COMPOSITION BY VOLUME.** Let x be percentage of nitrogen, then oxygen is $(100-x)$ m.l. (c. c.)

$$\text{Since } D = \frac{M}{V} \text{ or } M = V \times D,$$

Mass of x m.l. of Nitrogen $= 14 \times x$ and of $(100-x)$ m.l. (c. c.) of oxygen $= 16 [100-x]$

$$\text{Mass of 100 m. l. of mixture} = 100 \times 14.4 = 1440$$

Now, the sum of the masses of x m. l. of Nitrogen and $(100-x)$ m.l. of Oxygen must be equal to the mass of 100 m. l. of the mixture.

$$\therefore 14x + 16(100-x) = 1440.$$

$$\text{Or } 14x + 1600 - 16x = 1440, \text{ or } -2x = -160.$$

$$\text{Hence } x = 80.$$

The composition of mixture is : Oxygen $= 20\%$;

Nitrogen $= 80\%$;

(b) **Composition by weight.** Let ' p ' be the percentage by weight of Nitrogen.

$$\text{The volume of } p \text{ gms. of Nitrogen} = \frac{p}{14}$$

$$\text{The volume of } (100-p) \text{ gms. of Oxygen} = \frac{100-p}{16}$$

$$\text{Volume of 100 gms. of the mixture} = \frac{100}{14.4}$$

The sum of volumes of 'p' gms. of nitrogen and (100-p) gms. of oxygen must be equal to the volume of 100 gms. of the mixture.

$$\therefore \frac{p}{14} + \frac{100-p}{16} = \frac{100}{14.4} \quad \text{or } p=77.8.$$

The composition of the mixture is : Oxygen=22.2%,
Nitrogen=77.8%.

Problems.

1. Find the volume occupied by 50 gms of pure sulphuric acid of specific gravity 1.84.

2. 155 gms of a lead piece occupy a volume of 14.2 m. l. What is the density of the lead ?

3. 16.2 litres of oxygen measured at 0°C and one atmosphere pressure weigh 23.31 gms. Find the density of oxygen ?

4. A metallic block weighing 90 gms. in air is able to displace 60 m. l. of water. What is the density of the metal ?

5. Calculate the volume occupied by 50 gms. of bromine at 25°C. The specific gravity of bromine is 3.1.

6. 41.7 gms. of copper sulphate solution occupy the same volume as 42.3 gms of calcium chloride solution. Find the relative density of copper sulphate solution with respect to calcium chloride solution.

7. The specific gravity of alcohol is .75 and of a mixture of alcohol and water is 0.85. Calculate the composition of the mixture by volume.

8. The specific gravity of pure milk is 1.032 and of its mixture with water is 1.01. Calculate the composition of the mixture by volume.

9. The density of ozonised oxygen is 20 and of pure oxygen 16 and of ozone 24. Calculate the percentage

composition by volume of the sample.

10. The vapour density of sulphur dioxide is 32.0 and that of air relative to hydrogen is 14.4. Calculate the relative density of sulphur dioxide with respect to air.

11. The weight of a solid in water is 80 gms. and in another liquid is 88 gms. and in vacuum is 102.5 gms. Calculate the relative density of the liquid.

12. The percentage strength of acetic acid is 80 and its specific gravity is 1.25. Calculate the volume of the acid which will contain 25 gms, of the pure acid in it.

CHAPTER III

THE GAS LAWS

Introductory. Gases are a very dilute form of matter. They are very susceptible to changes in temperature and pressure. The volume of a gas changes in a very simple way with the variation of temperature and pressure. Some of the important gas laws are :—

Boyle's Law, Charles' Law, Graham's Law of diffusion of gases and **Dalton's law** of partial pressures.

1. **Boyle's Law** states that temperature remaining constant, the volume of a given mass of a gas is inversely proportional to the pressure. The volume increases with the decrease in pressure and vice versa. If the volume is doubled, the pressure is reduced to one-half, if the volume is made 4 times, the Pressure is reduced to one-fourth and so on. If P and V represent pressure and volume respectively then P varies as $\frac{1}{V}$.

If a pressure on a unit volume of a gas is changed from 1 to 2, 3, $\frac{1}{5}$, $\frac{1}{6}$ times, the volumes will change inversely as shown below :—

P	V	Product P. V.
1	1	$1 \times 1 = 1$
2	$\frac{1}{2}$	$2 \times \frac{1}{2} = 1$
3	$\frac{1}{3}$	$3 \times \frac{1}{3} = 1$
$\frac{1}{5}$	5	$\frac{1}{5} \times 5 = 1$
$\frac{1}{6}$	6	$\frac{1}{6} \times 6 = 1$

It is clear that in all these cases the product of

pressure and volume is the same or $PV = P_1 V_1 = P_2 V_2 = \dots = \text{constant}$.

EXAMPLE 1. *The pressure on 40 m. l. of a gas is changed from 760 mm to 800 mm. Find the new volume at the same temperature.*

$$P = 760 \text{ mm.}$$

$$P_1 = 800 \text{ mm.}$$

$$V = 40 \text{ m. l.}$$

$$V_1 = ?$$

$$\text{Since } PV = P_1 V_1$$

$$\therefore V_1 = \frac{PV}{P_1} = \frac{760 \times 40}{800} = 38 \text{ m. l.}$$

EXAMPLE 2. *Find the pressure at which 100 m. l. of a gas at 780 mm. pressure will occupy a volume of 130 m.l.*

$$P = 780 \text{ mm.}$$

$$P_1 = ?$$

$$V = 100 \text{ m.l.}$$

$$V_1 = 130 \text{ m.l.}$$

$$\text{Since } PV = P_1 V_1$$

$$\therefore P_1 = \frac{PV}{V_1} = \frac{100 \times 780}{130} = 600 \text{ mm}$$

Charle's Law states that pressure remaining constant, the volume of a given mass of a gas increases or decrease by $\frac{1}{273}$ of its volume at 0°C . for every 1°C rise or fall in temperature.

273 m.l. of a gas at 0°C . will change in volume with rise or fall in temperature thus :

273 m.l. of gas at 0°C . heated by 1°C . occupy a volume $= 273 + \frac{1}{273} \times 273 \text{ m.l.} = 274 \text{ m.l.}$

273 m.l. of gas at 0°C . cooled by $t^\circ\text{C}$. occupy a volume $= 273 - \frac{t}{273} \times 273 = (273 - t) \text{ m.l.}$

273 m.l. gas at 0°C . cooled by 273°C occupy a volume
 $=273 - \frac{273}{273} \times 273 = 0 \text{ m.l.}$

-273°C . is the temperature at which the volume of a gas would be zero. This hypothetical temperature is called **Absolute zero**.

All gases condense to liquids before this temperature is reached. In fact absolute zero temperature has not yet been obtained. Temperatures measured from Absolute zero are called Absolute temperatures. The Centigrade ($^{\circ}\text{C}$.) temperature is converted into Absolute temperature ($^{\circ}\text{A}$) by adding 273 to it because absolute zero is 273° below the Centigrade zero temperature.

Thus $27^{\circ}\text{C}. = 273 + 27 = 300^{\circ}\text{A}$. temperature

V_0 m.l. of a gas at 0°C . heated to $t_1^{\circ}\text{C}$. occupy =

$$V_0 + \frac{t_1}{27} \times V_0 = V_0 \left(\frac{273+t_1}{273} \right) \text{ l.m.}$$

V_0 m.l. of gas at 0°C heated to $t_2^{\circ}\text{C}$. occupy =

$$V_0 + \frac{t_2}{273} \times V_0 = V_0 \left(\frac{273+t_2}{273} \right) \text{ m.l.}$$

Let the volumes at t_1° and t_2° be Vt_1 and Vt_2 .

Then we have $Vt_1 = V_0 \left(\frac{273+t_1}{273} \right) \dots\dots(i)$

$$\text{and } Vt_2 = V_0 \left(\frac{273+t_2}{273} \right) \dots\dots(ii)$$

Dividing (i) by (ii)

$$\begin{aligned} \frac{Vt_1}{Vt_2} &= V_0 \left(\frac{273+t_1}{273} \right) \div V_0 \left(\frac{273+t_2}{273} \right) \\ &= \frac{273+t_1}{273+t_2} \dots\dots(iii) \end{aligned}$$

But $273+t_1$ and $273+t_2$ are absolute temperatures, T_1 and T_2 respectively.

$$\therefore \frac{V_{t_1}}{V_{t_2}} = \frac{T_1}{T_2}$$

Thus Charles' law can also be stated thus ; **Pressure remaining constant, the volume of a gas varies directly as the absolute temperature.**

EXAMPLE 3. 300 m.l. of a gas are heated from 27°C to 127°C . What will be the new volume of the gas at constant pressure ?

$$V_{t_1} = 300 \text{ m.l.}$$

$$T_1 = 273 + 27 = 300^\circ\text{A.}$$

$$V_{t_2} = ?$$

$$T_2 = 273 + 127 = 400^\circ\text{A}$$

$$\text{Since } \frac{V_{t_1}}{V_{t_2}} = \frac{T_1}{T_2}$$

$$\therefore V_{t_2} = \frac{V_{t_1} \times T_2}{T_1} = \frac{300 \times 400}{300} = 400 \text{ m.l.}$$

3. Relation between volume (V), temperature (T) and pressure (P) of a gas.

By Boyle's Law V varies as $\frac{1}{P}$ at constant temperature.

By Charles Law V varies as T at constant pressure.

Combining the two when T and P both change.

$$V \text{ varies as } \frac{T}{P}.$$

$$\text{Or } V = \frac{T}{P} \times \text{constant.}$$

$$= \frac{T}{P} \times R \text{ where } R \text{ is a constant}$$

$$\therefore \frac{PV}{T} = R, \text{ or } PV = RT.$$

This is known as the Gas Equation. It follows that

$\frac{PV}{T}$ is constant for different values of P, V and T.

$$\text{Or } \frac{PV}{T} = \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_3} \text{ etc.}$$

Thus if the volume of a gas at a particular temperature and pressure be given, the volume at another temperature and pressure can be calculated. The different quantities of gases can be conveniently compared by reducing them to a standard temperature and pressure. Thus 0°C , and 760 mm. pressure are taken as the **standard** or Normal temperature and pressure and are briefly denoted by **S. T. P.** or **N. T. P.** respectively.

EXAMPE 4. *What volume will 60 litres of a gas at 17°C and 750 mm. pressure, occupy at S. T. P.*

$$P = 750 \text{ mm.} \quad P_0 = 760$$

$$V = 60 \text{ litres} \quad V_0 = ?$$

$$T = 273 + 17 = 290^\circ\text{A} \quad T_0 = 273.$$

$$\text{Since } \frac{PV}{T} = \frac{P_0 V_0}{T_0} \therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\text{or } \frac{750 \times 60}{290} \times \frac{273}{760} = 55.7 \text{ litres.}$$

EXAMPLE 5. *100 m.l. of Nitrogen collected at 27°C and 720 mm. are cooled to -73°C . under pressure of 760 mm. What is the volume occupied by it?*

$$P = 720 \text{ mm.} \quad P_1 = 760 \text{ mm.}$$

$$V = 100 \text{ m.l.} \quad V_1 = ?$$

$$T = 300^\circ\text{A.} \quad T_1 = 200^\circ\text{A. i.e. } (273 - 73 = 200^\circ\text{A.})$$

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1}$$

$$V_1 = \frac{PV}{T} \times \frac{T_1}{P_1} = \frac{720 \times 100}{300} \times \frac{200}{760} = \frac{1200}{19} = 63.1 \text{ m.l.}$$

EXAMPLE 6. Find the weight of one litre of Hydrogen measured at 37°C . and 800 mm. pressure. (One litre of Hydrogen at N. T. P. weighs .09 gm.)

$$P=800 \text{ mm.}$$

$$P_0=760 \text{ mm.}$$

$$V=1000 \text{ m.l.}$$

$$V_0=?$$

$$T=310^{\circ}\text{A.}$$

$$T_0=273\text{A.}$$

$$\frac{PV}{T} = \frac{P_0V_0}{T_0}$$

$$\therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\text{Or } \frac{800 \times 1000 \times 273}{760 \times 310} = 927 \text{ m.l.}$$

1000 m.l. Hydrogen at N. T. P. weigh .09 gm.

927 m.l. Hydrogen at N. T. P. weigh $\frac{927 \times .09}{1000}$

= .083 gms.

4. Dalton's law of Partial Pressures states that in a mixture of gases, the total pressure P is equal to the sum of the partial pressure (p_1, p_2, p_3 , etc) of the constituents. This means that the pressure exerted by a gas in an enclosed space is independent of the presence of any other gas or vapour in that space.

The space above the surface of a liquid always contains vapour of the liquid because slow evaporation is always going on. When a gas like hydrogen is collected over water the pressure exerted on the liquid is due to the gas plus the water vapour. This vapour pressure is also called vapour tension or aqueous tension. The true pressure exerted by the gas is therefore obtained by allowing for the vapour tension. Vapour pressure of mercury is negligible.

EXAMPLE 7. 100 m.l. of hydrogen are collected over

water at 27°C and 726.5 mm. pressure. Calculate the volume of the dry gas at S.T.P. (vap. tension at 27°C . = 26.5 mm.)

$$P \text{ dry gas} = 726.5 - 26.5 = 700 \text{ mm.} \quad P_0 = 760 \text{ mm.}$$

$$V = 100 \text{ m.l.} \quad V_0 = ?$$

$$T = 273 + 27 = 300^{\circ}\text{A.} \quad T_0 = 273.$$

$$\frac{P_0 V_0}{T_0} = \frac{PV}{T}$$

$$\therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0} = \frac{700 \times 100 \times 273}{760 \times 300} = \frac{19110}{228} = 83.8 \text{ m.l.}$$

5. Graham's Law of Diffusion of Gases :—

Under the same condition of temperature and pressure the rates of diffusion of gases are inversely proportional to the square roots of their densities. Or

$$\frac{R_1}{R_2} = \sqrt{\frac{d_2}{d_1}}$$

When $R_1 R_2$ and $d_1 d_2$ are the rates of diffusion and densities of two gases respectively.

Two or more gases when brought in contact with one another, the particles of gases tend to mix in all proportions to form a homogeneous mixture. The rates of diffusion depend on their densities.

N. B.—As time is inversely proportional to rates, the relationship between the densities of the gases and the time that their equal volume will take to diffuse will

be denoted as $\frac{t_1}{t_2} = \sqrt{\frac{d_1}{d_2}}$. So that we have the relation-

$$\text{ship } \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$$

EXAMPLE 8. 100 m.l. of chlorine diffuse in the same time in which 120 c. c. of ozone diffuse. The density of chlorine is 35.5. Find the density of ozone.

$$\frac{R_1}{R_2} = \sqrt{\frac{D_2}{D_1}} \text{ where } R_1 \text{ and } D_1 \text{ are the rate of diffusion}$$

and density of chlorine and R_2 and D_2 those of ozone.

$$\therefore \frac{100}{120} = \sqrt{\frac{D_2}{35.5}} \text{ or } \frac{100 \times 100}{120 \times 120} = \frac{D_2}{35.5}$$

$$\therefore D_2 = \frac{100 \times 100 \times 35.5}{120 \times 120} = 24.6.$$

Problems.

1. What will be the volume occupied by 500 m.l. of a gas under a pressure of 740 mm. if the pressure is increased to 760 mm.

2. What volume will 100 m.l. of oxygen measured at a pressure of 760 mm. occupy at 770 mm. and 730 mm. respectively?

3. Find the volume that:—

(a) 150 m.l. of a gas at 18°C. will occupy at 25°C.

(b) 300 m.l. of a gas at 28°C. will occupy when cooled to -14°C?

4. At what Centigrade temperature will 1.3 litres of hydrogen at 0°C occupy a volume of 2 litres?

5. Find the volume occupied by:—

(a) 20 m.l. of gas at 15°C and 770 mm. if the temperature is raised to 30°C and pressure to 780 mm.

(b) 50 m.l. of air at 27°C and 750 mm. if the temperature is raised to 77°C. and pressure to 1000 mm.

(c) 100 m.l. of oxygen collected over water at 17°C and 750 mm. If temperature is lowered to 0°C . and pressure is raised to 760 mm. (Aq. tension at 17°C . = 14 mm.)

6. (a) What volume will 46 m.l. of a gas 24°C . and 755 mm. occupy at S. T. P. ?

(b) 146 m.l. of air at 17°C and 974 mm. are heated to 51°C . and the pressure is decreased to 760 mm. What will be the new volume of air ?

7. Find the pressure at which 1000 m.l. of air at 0°C and 600 mm. will occupy 1895.6 m.l. when heated to 72°C .

8. At what temperature will 20 m.l. of oxygen at 27°C . and 782 mm. collected over water will occupy half the volume (collected over mercury) if the pressure is raised to 1270 mm. (Aq. tension at 27°C = 20 mm.)

9. The rates of diffusion of ozone and carbon dioxide are 27 : 28. The relative density of ozone is 24, calculate that of carbon dioxide.

10. 71 m.l. of carbon dioxide diffuse in the same time in which 89 m.l. of carbon monoxide do. The density of carbon dioxide is 22. Find the density of carbon monoxide.

11. 30 m.l. of ozone diffuse in the same time as 25 m.l. chlorine. If density of chlorine is 35.4, find that of ozone.

12. The relative densities of two gases A and B are 1 : 1.05. Find the number of m.l. of B which will diffuse in the same time in which 150 m.l. of A would diffuse.

13. A glass globe is filled with air at 760 mm. and 30°C . and then sealed. On heating the globe bursts at 450°C . What pressure can the walls of the bulb withstand ?

14. 115 m.l. of carbon monoxide were collected over water at 30°C . and 767 mm. On reducing the temperature to 20°C . the volume was reduced to 10 m.l. Find the pressure on the gas. (Aq tension at $30^{\circ}\text{C} = 30$ mm.)

15. What volume of ammonia at 30°C . and 760 mm. must be passed through 200 gms. of a 5 percent solution of hydrochloric acid in order to neutralise it completely if 36.5 gms. of hydrochloric acid require 22.4 litres of ammonia at S.T.P. for complete neutralisation?

16. A flask has a capacity of 500 m.l. What volume air will escape from the flask if it is warmed from 25°C . to 35°C and the barometric remains unchanged. Neglect the expansion of glass. (*Patna Inter 1929*)

17. What will be the volume at N.T.P. of 76.0 m.l. moist nitrogen measured at 16°C . and 753.5 mm. pressure [Aq. tension at $16^{\circ}\text{C} = 13.5$ mm.] (*P. U. 1936*)

18. In 50 seconds, 300 m.l. of oxygen diffuse through a porous plate. How long will it take 500 m.l. of chlorine to diffuse through the same plate? Take the molecular weight of oxygen and chlorine as 32 and 71, respectively. (*London Gen. School*)

19. A gas was allowed to diffuse into air through a porous diaphragm, pressure on both sides of the diaphragm being equal throughout the experiment. The volume of air which entered was 15 m.l. and the volume of gas which escaped was 15.21 m.l. What was the density of the gas in question compared with that of air? (*U. P. board inter*)

20. If 16 m.l. of hydrogen diffuse in 100 seconds, what volume of SO_2 will diffuse in the same time under similar condition? (*U. P. Board Inter 1918*)

21. The rates of diffusion of ozone and chlorine are as 6 : 5. Assuming the density of chlorine as 36 find the molecular formula of ozone. (*Nagpur Inter. 1931*)

22. Calculate the volume of Nitric Oxide which will diffuse out of a porous partition in ten seconds, when 25 m.l. of marsh gas (CH_4) come out in 4 seconds.

(U. P. Board Inter)

23. Sulphuric Dioxide is 2.048 times heavier than Oxygen. Find out how much Oxygen will diffuse in the same time as 50 m.l. of the other gas.

(Bombay Univ Inter)

24. The speeds of diffusion of carbon dioxide and of ozone were found to be as 0.58 : 0.542 ; find the molecular weight of ozone if that of carbon dioxide is known.

(Punjab B. Sc. 1944)

25. The speeds of diffusion of carbon dioxide and ozone were found to be as 0.29 is to 0.274. The relative density of CO_2 is 22 when $\text{H}_2=1$. What is the relative density of ozone ?

(U. P. Board Inter 1946)

26. The relative rate of diffusion of a gas as compared with carbon dioxide is as 27 : 29. Calculate the relative density of the gas, that of carbon dioxide being 22.

(Calcutta Inter 1934)

27. Calculate the molecular weight of an unknown gas which under precisely similar conditions takes 1.117 times as long as oxygen to diffuse through an aperture.

(Punjab B. Sc. 1924)

Density of air relative to hydrogen = 14.4

28. How many mililitres of hydrogen will pass through a porous plug in the same time as 2 m.l. of air ?

(Allahabad, 1923)

29. 180 m.l. of a hydrocarbon diffuse in 15 minutes while under similar conditions 120 m.l. of sulphur dioxide diffuse in 20 minutes. If the molecular weight of SO_2 is 64, what is the molecular weight of the hydrocarbon ?

(Nagpur Inter 1933)

30. If 50 volumes of hydrogen take 85 seconds to diffuse from a vessel, how long would it take 35 volumes of nitrous oxide to do so under the same conditions?

(*U. P. Board Inter 1936*)

31. The relative rates of diffusion of a gas as compared with that of carbon dioxide is as 266 : 218. Calculate the molecular weight of the gas. (*U. P. Board Inter 1940*)

32. The speeds of diffusion of carbon dioxide and of ozone were found to be as 0.29 to 0.271. The relative density of carbon dioxide is 22 when $H=1$. What is the relative density of ozone? (*U. P. Board Inter 1930*)

33. The density of oxygen is 16 and that of nitrogen is 14 at 0°C and 760 m.m. At what temperature will oxygen have the same density as nitrogen at 0°C assuming that the pressure remains constant?

(*Punjab Inter 1938*)

34. A volume of hydrogen measures one cubic decilitre at 20°C and of pressure of half an atmosphere. How many m.l. will it occupy at 10°C and under 700 mm. pressure? (*U. P. Board Inter 1903*)

35. 400 m.l. of oxygen are collected over water at 17°C . and under 750 mm. Pressure. What will be the volume of the dry gas under standard conditions? (Tension of aqueous vapour at 17°C is 14.4 mm.)

36. When the pressure is 735 mm. and the temperature 27°C . the volume of gas is 2895 m.l. What will be the volume of the same gas in litres at N. T. P.

(*U. P. Board Inter*)

37. 110 m.l. of hydrogen were collected over water at 18°C and 740 mm. pressure. Calculate the volume of the gas at normal temperature and pressure (a) taking

account of the pressure of water vapour = 15.4 mm. at 18°C. (b) neglecting the effect of water vapour.

. (*Cambridge School Certificate*)

38. 50 m.l. of H_2 at N.T.P, were confined in a tube of cross section 1.2 sq cm. and standing in a trough of mercury, the column of which stood at a height of 15 cm. The pressure was now changed to 750 m.m. and the temperature to 31°C. Find the length of column of tube containing the gas. (*Calcutt Inter. 1941*)

39. 100 m.l. of nitrogen collected at 27°C and 720 mm. are cooled to -73°C under a pressure of 760 mm. What is the volume occupied by it? (*Delhi Inter 1940*)

CHAPTER IV

LAWS OF CHEMICAL COMBINATION

There are five Laws of Chemical Combination :—

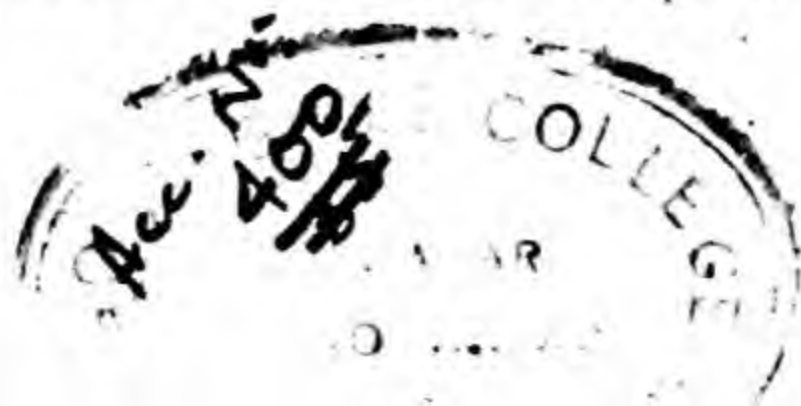
1. **The Law of Conservation of Matter.**
2. **The Law of Constant Proportions.**
3. **The Law of Multiple Proportions.**
4. **The Law of Combining Weights.**
5. **Gay-Lussac's Law of Volumes.**

1. **The law of conservation of matter. In a chemical reaction the total mass of the system remains constant.**

The law can be proved by showing that the weight of the products formed is equal to the weight of the reacting substances. Thus a λ tube containing silver nitrate solution in one arm and potassium chromate solution in the other, is weighed and then the two solutions are mixed to form silver chromate and potassium nitrate. The tube is weighed again and is found to have the same weight.

2. **The Law of Constant proportions. A Chemical Compound always contains the same elements combined together in the same ratio by weight.**

Silver chloride can be prepared from silver by different methods and if the various samples are analysed, they will always contain 108 parts of silver for 35.5 parts of chlorine to form 143.5 parts of silver chloride, therefore it is said that the same compound may be prepared by various methods but the samples formed will always contain the same elements combined in the same ratio.



EXAMPLE 1. *Zinc oxide prepared from zinc by different methods gave the following results :—*

(i) 3.27 gms. of zinc dissolved in sulphuric acid, precipitated as hydroxide and ignited, gave 4.05 gms. of zinc oxide.

(ii) 2.472 gms. of zinc dissolved in nitric acid and nitrate ignited leave behind 3.076 gms. of zinc oxide.

(iii) 2.16 gms. of zinc dissolved in an acid, precipitated as carbonate and ignited leave behind 2.68 gms. of zinc oxide.

Show that they justify the above law.

(1) 3.27 gms. of zinc combine with $4.05 - 3.27$ or 0.78 gms. of oxygen.

\therefore 0.78 gms. of oxygen combine with 3.27 gms. of zinc.

Or Ratio of oxygen to zinc is $0.78 : 3.27$ or $1 : 4.1$.

(ii) 2.472 gms. of zinc combine with $3.076 - 2.472$ or 0.604 gms of oxygen.

Or 0.604 gms of oxygen combine with 2.472 gms. of zinc.

\therefore oxygen : zinc as 0.604 : 2.472 or $1 : 4.09$.

(iii) 2.16 gms. of zinc combine with $2.68 - 2.16$ or 0.52 gms. of oxygen.

Or 0.52 gms. of oxygen combine with 2.16 gms. of zinc.

\therefore oxygen : zinc as 0.52 : 2.16 or $1 : 4.1$.

Since in all the three cases ratio of oxygen to zinc is the same *i.e.* $1 : 4.1$, therefore the law of constant composition holds good.

3. The Law of Multiple proportions. When two elements combine to form two or more compounds, the weights of one of the elements which combine with a fixed weight of the other are in a simple ratio to one another.

EXAMPLE 2. 1.023 gms of mercuric oxide and 1.895 gms. of mercurous oxide leave behind 0.9473 gms. and 1.822 gms. of mercury respectively. How can the law of multiple proportions be illustrated with this data.

(i) 0.9473 gms. of mercury combine with 0.0757 gms. of oxygen,

$$\therefore \frac{\text{oxygen}}{\text{mercury}} = \frac{0.0757}{0.9473} = \frac{0.0798}{1}$$

(ii) 1.822 gms. of mercury combine with 0.0728 gms. of oxygen,

$$\therefore \frac{\text{oxygen}}{\text{mercury}} = \frac{0.0728}{1.822} = \frac{0.0399}{1}$$

But $0.0798 : 0.0399 :: 2 : 1$, therefore the law holds good in this case.

EXAMPLE 3. It has been found that 5.6 gms of nitrogen combine with oxygen to form 8.8 gms. of nitrous oxide, 12 gms. of nitric oxide 15.2 gms. of nitrogen trioxide, 18.4 gms. of nitrogen peroxide and 21.6 gms. of nitrogen pentoxide. Show that these illustrate the Law of Multiple Proportions.

5.6 gms. of nitrogen form nitrous oxide by combining with 3.2 gms. of oxygen.

5.6 gms. of nitrogen form nitric oxide by combining with 6.4 gms. of oxygen.

5.6 gms. of nitrogen form nitrogen trioxide by combining with 9.6 gms. of oxygen.

5.6 gms. of nitrogen form nitrogen peroxide by combining with 12.8 gms. of oxygen.

5.6 gms. of nitrogen form nitrogen peroxide by combining with 16.0 gms. of oxygen.

The wts. of oxygen combining with the same weight of nitrogen are to one another as :—

$$3.2 : 6.4 : 9.6 : 12.8 : 16.0.$$

$$\text{Or } 1 : 2 : 3 : 4 : 5.$$

Hence the wts. of oxygen bear simple ratio to one another.

EXAMPE 4. *The black and red oxides of copper contain 79.9% and 88.3% copper. Lead monoxide and dioxide contain 92.8% and 86.6% lead respectively. Establish the law of multiple proportion from this Data.*
(P. U. 1921)

In black copper oxide percentage of copper is 79.9 p.c
oxygen is 20.1 p.c

20.1 parts oxygen combine with 79.9 parts copper,

$$\therefore 1 \quad \text{..} \quad \text{..} \quad \text{..} \quad \text{..} \quad \frac{79.9}{20.1} = 3.975 \text{ copper}$$

Or **oxygen** is to **copper** as **1 : 3.975**.....(I)

In red oxide percentage of copper is 88.3 and of oxygen is 11.7.

Or 11.7 parts oxygen combine with 88.3 parts copper

$$\therefore 1 \quad \text{..} \quad \text{..} \quad \text{..} \quad \text{..} \quad \frac{88.3}{11.7} = 7.547 \text{ parts}$$

copper.

Or oxygen : copper as 1:7.547.....(II)

It is clear that proportion of copper in I and II is 3.975 : 7.547 or 1:2.

In lead monoxide percentage of lead is 92·8 and of oxygen is 7·2

7·2 parts oxygen combine with 92·8 parts lead.

$$1 \text{ " " " " } \frac{92\cdot8}{7\cdot2} = 12\cdot89 \text{ lead ... (A)}$$

In lead peroxide %age of lead is 86·6 and oxygen is 13·4

Or 13·4 parts oxygen combine with 86·6 parts lead.

$$\text{ " " " " " } \frac{86\cdot6}{13\cdot4} = 6\cdot46 \text{ lead ... (B)}$$

The wts of lead in the two oxides are to one another as 12·89 : 6·46 or 2 : 1.

IV. Law of Equivalent weights. It states that the weights of different elements which combine with a definite weight of another element are either the same or simple multiple or submultiple of the ratio in which these different elements combine with each other.

The law can be better illustrated with the help of examples. Thus taking the case of sulphur dioxide and sulphuretted hydrogen the ratio in which the elements combine are :—

Sulphur dioxide S : O as 32 : 32.

Sulphuretted Hydrogen S : H as 32 : 2.

Now if hydrogen and oxygen combine together, they will do so in the ratio 2 : 32 or its multiple or submultiple.

Thus in water, hydrogen and oxygen combine in the ratio 2 : 16.

Similarly in carbon dioxide and methane (CH₄) the proportions are :—

Carbon dioxide—C : O as 12 : 32.

Methane—C : H as 12 : 4.

Therefore hydrogen and oxygen will combine in the ratio 4 : 32 or 1 : 8 and so they do in case of water.

The law can also be stated as follows:- **When substances (elements or compound) react together they always do so in the ratios of their equivalent weights**, where in equivalent weight of a substance is defined to be the number of parts by weight of it which react, directly or indirectly with 1 part by weight of hydrogen or 8 parts by weight of oxygen.

EXAMPLE 5. *The percentage composition of the following compounds is given to be :—*

Carbon dioxide $\left\{ \begin{array}{l} \text{C} = 27.27\% \\ \text{O} = 72.73\% \end{array} \right.$

Methane $\left\{ \begin{array}{l} \text{C} = 75\% \\ \text{H} = 25\% \end{array} \right.$

Water $\left\{ \begin{array}{l} \text{H} = 11.12\% \\ \text{O} = 88.88\% \end{array} \right.$

Illustrate the law of equivalents.

Since in methane 75 parts carbon combine with 25 parts hydrogen.

27.27 parts carbon combine with $\frac{27.27 \times 25}{75} = 9$ parts H.

\therefore the weights of hydrogen and oxygen combining with the same weight 27.27 of carbon are 9 : 72.73 or 1 : 8.

While in water also hydrogen and oxygen combine in the ratio 11.12 : 88.88 or 1 : 8.

Thus the law is supported by these data.

Problems

1. In two experiments the following results were obtained :—

(i) 7.911 gms. of silver chloride on reduction with dry Hydrogen left behind 5.958 gms silver.

(ii) In the other case 5.736 gms. silver was dissolved in nitric acid and precipitated as chloride with sodium chloride solution. The silver chloride was washed, dried and weighed to be 7.614 gm.

How would you show that these results prove the law of constant proportion.

2. 2.465 gms. of cupric oxide were reduced with hydrogen and copper left was found to weigh 1.9764 gms.

In another experiment 1.945 gms. of copper were dissolved in nitric acid and the nitrate was decomposed by strong heating to form the copper oxide which was found to weigh 2.435 gm.

Show that these results illustrate the law of definite composition.

3. Justify the law of multiple proportion from the following percentage composition of two oxides of carbon :—

	(1)	(2)
Carbon	42.86	27.27
Oxygen	57.14	72.73.

4. In four experiments the following percentage composition of four hydrocarbons was found :—

I	II	III	IV
C=75	80	85.7	92.3.
H=25	20	14.3	7.7.

Illustrate the Law of multiple proportion from the above data.

⑤ The percentages of chlorine in tri and penta chlorides of phosphorus are 77.45 and 85.13 respectively.

How will you show that they are in harmony with the law of Multiple proportion.

6. In three experiments the following weights of Litharge, lead peroxide and red lead were reduced in a current of hydrogen : 2.173 gms., 1.949, and 2.316 gms. The weights of lead left in each case are 2.017 gms., 1.688 gms. and 2.100 gms. respectively. Illustrate the law of multiple proportion from the above. (P. U. 1924).

7. Illustrate the law of chemical equivalents from the following percentage composition :—

(a) In carbon dioxide, carbon bisulphide and sulphur dioxide

$$C = 27.27\%$$

$$C = 15.8$$

$$S = 50.$$

$$O = 72.73\%$$

$$S = 84.2$$

$$O = 50.$$

(b) In phosphoric phosphorous trichloride and hydrochloric acid.

$$P = 91.18$$

$$P = 22.55.$$

$$H = 2.78.$$

$$H = 8.12$$

$$Cl = 77.45.$$

$$Cl = 97.22.$$

8. Prove the law of reciprocal proportion from the data given below.

In Ferric oxide In Ferric chlorine In chlorine peroxide

$$Fe = 61.94\%$$

$$Fe = 34.46$$

$$Cl = 52.56$$

$$O = 38.06$$

$$Cl = 65.53$$

$$O = 47.44$$

9. Justify the law of equivalent weights if the percentage composition given are :—

In silver chloride In chlorine monoxide In silver oxide

$$Ag = 75.26$$

$$Cl = 81.59$$

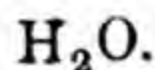
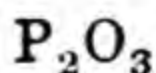
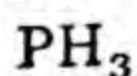
$$Ag = 93.1$$

$$Cl = 24.74$$

$$O = 18.41$$

$$O = 6.9$$

10. The percentage composition of three compounds is given below. Prove the law of equivalent weights from it :—



$$P = 91.18$$

$$P = 56.36$$

$$H = 11.11.$$

$$H = 8.82.$$

$$O = 43.63,$$

$$O = 88.89.$$

11. On analysis it was found that the black oxide of copper, the red oxide of copper, litharge, the red oxide of lead, the peroxide of lead contain 79.79%, 88.3%, 92.3%, 90.6% and 86.6% respectively of the metal. Establish the law of multiple proportions with the help of these data.

12. An element forms two oxides containing respectively 53.33 and 36.36% of oxygen. Show that these figures illustrate the Law of Multiple Proportions.

13. If a certain oxide of nitrogen weighing 11 gms. yields 5.6 litres of nitrogen and another oxide of nitrogen weighing 15 gms yield also the same volume of nitrogen (all measurements being made at N. T. P.), show that the data cited support the law of multiple proportions.

(U. P. Board Inter 1925)

14. A metal M forms two chlorides. One contains 35.86% of chlorine and 64.14% of M; the other contains 52.79% of chlorine and 47.21% of M. Use the numbers to illustrate the law of multiple proportions.

(P. U. Board Inter 1925)

15. Analysis of two oxides of mercury gave the following result :—

1.023 gms. of mercuric oxide gave 56.2 m.l. of oxygen measured at 15°C and 750 m.m. pressure. 1.895 gms. of mercurous oxide gave 54.1 m.l. of oxygen at 14°C and 447 m.m. pressure show that these results are in agreement with the law of multiple proportions.

(P. U. 1917)

16. Stas found that 1.0 gm. of carbon yielded 3.7 gms. of carbon dioxide. When the lower oxide of carbon was passed over heated copper oxide, he found that 61.9 gms. of carbon dioxide were formed and that the diminution in the weight of copper oxide was 22.5 gms. Deduce the percentage composition of the lower oxide and show

that the results are in agreement with the law of multiple proportions.

(U. P. Board Inter 1917)

17. A metal is found to give two oxides. On heating 1.0 gm. of each in a current of hydrogen. 0.798 gms. and 0.888 gms. of the metal are obtained. Show that these results are in agreement with the law of the multiple proportions.

(Benaras Inter 1927)

18. Show that the law of multiple proportions is illustrated by the fact that the chlorides of mercury contain respectively 26.20% and 15.08% of chlorine.

19. Specimens of two hydrocarbons were burnt in an excess of oxygen. 0.016 gm. of the one gave 23.9 m.l. of CO_2 and 0.052 gm. of the other gave 95.8 m.l. of CO_2 both volumes being at 15° and 755 m.m. pressure. Show that these figures are in agreement with the law of multiple proportions.

(U. P. Board Inter 1944)

20. Illustrate the law of multiple proportions by reference to the three compounds of the elements A and B which contain respectively 25.0% ; 14.28% ; 7.69% of B.

(U. P. Board Inter 1914)

21. Four oxides of lead on analysis gave the following results :—

<i>Oxide</i>	<i>Lead</i>	<i>Oxygen</i>
Suboxide	4.144 gms.	0.160 gm
Monoxide	1.036 gms.	0.080 gm.
Sesquioxide	5.180 gms.	1.600 gms.
Peroxide	6.488 gms.	1.002 gms.

Establish the law of multiple proportions with the above results.

(P. U. 1931)

22. State the law of multiple proportion. Show how this law is illustrated by a case where an element from two oxides containing 53.33% and 36.36% of oxygen respectively.

(Rajputana Inter 1937)

23. Two oxides of a metal M contain respectively 22.53% and 30.38% of oxygen. If the formula of the first oxide is M.O, what will be the formula of the second ?

24. On analysis it was found that the black oxide of copper, the red oxide of copper, litharge, the red oxide of lead, and the peroxide of lead contain 79.9%, 88.8%, 92.8%, 90.6%, 86.6% respectively of metal. Establish the law of multiple proportion with the help of these data.

(Punjab Inter 1931)

25. Phosphine (PH_3) contains 91.1% of phosphorus and 8.9% of Hydrogen water (H_2O) contains 88.8% of oxygen and 11.2% of hydrogen ; and P_4O_6 contains 56.4% of phosphorus and 43.6% of oxygen. Show without using the atomic weights that the data illustrate the law of reciprocal proportions.

(Bombay Inter 1934)

CHAPTER V

DETERMINATION OF EQUIVALENT WEIGHTS

(OR COMBINING WEIGHTS)

DEFINITION :—The combining weight or the equivalent weight of a substance (Element or Compound) may be defined as the number of parts by weight of it which combine with or displace from combination 8 parts by weight of oxygen or 1.008 parts by weight of hydrogen.

Since 9 grams of aluminium, 12 grams of magnesium, 28 grams of iron can combine with 8 grams of oxygen or can displace 1.008 gram of Hydrogen from acids, therefore 9.12 and 28 are the equivalent weights of aluminium, magnesium and iron respectively. The determination of equivalent weight can be done by a suitable reaction in which the substance concerned take part. The following are different methods used for finding the equivalent weights of metals :—

METHOD I. Hydrogen displacement method. This method is used for determining the equivalent weights of the metals (Zn, Fe, Mg.) which on reaction with acids evolve Hydrogen. In this method a known weight of the metal is treated with an excess of acid and the volume of hydrogen evolved is measured. The temperature and pressure at which the experiment is carried on, are noted. From this data the volume of hydrogen at N. T. P. is calculated and its weight determined. From the weight of the metal which can liberate 1 gm. of hydrogen is determined.

EXAMPLE 1. *212 gm. of magnesium were dissolved in dilute hydrochloric acid and the volume of hydro-

gas collected over water at 16°C and 750 m.m. pressure was 213.5 m.l. Calculate the equivalent weight of the metal. (Aq. tension at 16°C 13.5 mm.)

Wt. of mg = .212 gm.

$$P_0 = 760 \text{ mm} \quad P_1 = 750 - 13.5 = 736.5.$$

$$V_0 = ? \quad V_1 = 213.5 \text{ m.l.}$$

$$T_0 = 273\text{A.} \quad T_1 = 289\text{A.}$$

$$\frac{P_0 V_0}{T_0} = \frac{PV}{T} \quad \therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\text{Or } V_0 = \frac{736.5 \times 213.5 \times 273}{289 \times 760} = 195.2 \text{ m.l.}$$

1 m.l. H at N. T. P. weighs .00009 gm.

$$195.2 \text{ ,, ,, ,, } = .00009 \times 195.2 = .017568.$$

.01757 gm. Hydrogen is displaced by .212 gm. magnesium

$$\therefore 1 \text{ gm. Hydrogen is displaced by } \frac{1 \times .212}{.01757} =$$

12.07 gms. Mg.

Eq. wt. of Mg. = 12.07 Ans.

METHOD II. Metal displacement method. In this method metals whose equivalent weights are to be determined are displaced from solutions of their salt by some suitable metal of known equivalent weight.

Thus magnesium, iron and zinc can displace copper from copper sulphate solution and zinc can displace silver from silver nitrate solution. If about .2 gm. of magnesium is placed in copper sulphate solution, magnesium will go in solution and copper will be precipitated. The weight of precipitated copper is determined. If the equivalent of magnesium is given, that of copper can be determined, because the weights will be in the ratio of their equivalent weights.

Wt. of mg. = 2.0 gms. Wt. of oxide = 3.33 gms.

\therefore oxygen used = 1.33 gm. (3.33—2) gms.

1.33 gms. oxygen combines with 2 gms. magnesium.

\therefore 8 gms. oxygen combines with $= \frac{2 \times 8}{1.33} = 12.03$ gms.

\therefore Eq. Wt. of Mg = 12.03

EXAMPLE 4. 3.54 gms. of copper were dissolved in excess of concentrated nitric acid and the nitrate thus formed was ignited strongly to form the oxide. The weight of the oxide formed was 4.44 gms. Find the equivalent weight of copper.

Wt. of the oxide = 4.44 gms.

Wt. of the metal = 3.54 gms.

Wt. of oxygen used = .9 gms.

Thus .9 gms. oxygen combines with 3.54 gms. copper.

\therefore 8 gms. Oxygen combines with $\frac{8 \times 3.54}{.9}$
= 31.45 gm.

Or Eq. wt. of Cu = 31.45.

EXAMPLE 5. 112.4 m.l. of oxygen at 15°C. and 750 mm. pressure were evolved by heating 2.046 gms. of mercuric oxide. Calculate the equivalent weight of mercury.

$P_0 = 760$ mm.

$P_1 = 750$ mm.

$V_0 = ?$

$V_1 = 112.4$ c.l.

$T_0 = 273$

$T_1 = 273 + 15 = 288$

Since $\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$

$\therefore V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$

$= \frac{750 \times 112.4 \times 274}{288 \times 760} = 105.0$ m.l.

1 m.l. of oxygen at N. T. P. weighs $= .00009 \times 16$
 $= .00144$ gm.

105 m.l. of oxygen at N. T. P. weigh $= .00144 \times 105$
 $= .1512$ gms.

Wt. of mercury oxide $= 2.046$ gm.

„ oxygen obtained $= .1512$ gms.

„ mercury $= 1.8948$ gms.

.1512 gm. oxygen will combine with 1.8948 gm Hg.

$$\therefore 8 \text{ gms. oxygen will combine} = \frac{8 \times 1.8948}{.1512}$$

$$= \frac{15.1584}{.1512} = 100.2$$

Eq. Wt. of Hg. $= 100.2$.

(b) **By conversion into the chloride.**

A known weight of the metal is changed into its chloride and the weight of chloride formed obtained.

The equivalent weight of chlorine being 35.5, the weight of the metal that will combine with 35.5 gms. of chlorine is calculated and it is equal to the equivalent weight.

EXAMPLE 6. *In excess of nitric acid 2.4 gms of silver were dissolved and the nitrate solution was treated with excess of common salt solution to precipitate completely the silver chloride. The precipitate was filtered, washed, dried and weighed to be 3.19 gms. Determine the equivalent weight of silver that of chlorine is 35.5.*

Wt. of silver is 2.4 gms.

Wt. of silver chloride $= 3.19$ gms.

Wt. of chlorine used $= .79$ gm.

.79 gms, chlorine combines with 2.4 gms. silver.

$$35.5 \text{ gms. chlorine combines with } \frac{2.4 \times 35.5}{.79} = \frac{85.70}{.79} = 107.85 \text{ gms.}$$

METHOD IV. Reduction Method. This method depends on the reduction of the oxide of the metal with hydrogen. A current of pure dry hydrogen is passed over a weighed quantity of the heated oxide and the metal left behind on reduction is weighed, or the water formed is determined.

EXAMPLE 7. *A current of dry hydrogen is passed over 2.214 gms. of copper oxide and the metal obtained on reduction weighed 1.7685 gms. Calculate the equivalent weight of copper.*

Wt. of copper oxide = 2.214 gms.

Wt. of copper left = 1.7685 gms.

∴ Wt. of oxygen = .4455 gm.

.4455 gms. oxygen were combined with 1.7685 gms. of copper.

$$\begin{aligned} \therefore 8 \text{ gms. oxygen were combined with} &= \frac{1.7685 \times 8}{.4455} \\ &= \frac{14.1480}{.4455} = 31.8. \end{aligned}$$

∴ Eq. Wt. of copper is = 31.8.

METHOD V. By double decomposition. A solution of weighed quantity of a salt is treated with excess of solution of another salt to precipitate a third salt formed during double decomposition. The precipitate is filtered, washed, dried and weighed. If equivalent wts. of two radicals are given that of the third can be calculated. The following example will make it clear.

EXAMPLE 8. *9.989 gm. of sodium chloride were dissolved in water and silver nitrate solution was added*

in excess. The precipitate of silver chloride was thoroughly washed, dried and weighed to be 2.42 gms. Calculate the equivalent weight sodium those of silver and chlorine being 108 and 35.5 respectively. —

$$\text{Sol.:-} \quad \frac{x + 35.5}{108 + 35.5} = \frac{.989}{2.42}$$

$$\therefore 2.42 x = .989 \times 143.5 - 2.42 \times 35.5 \\ = 141.9215 - 85.91 = 56.0115.$$

$$\therefore x = \frac{56.0115}{2.42} = 23.1 = \text{Eq. Wt. of sodium}$$

METHOD VI. (By Electrolysis) Equivalent weights can also be determined by electrolysis of solution of salts of different metals in voltameters connected in series. Faraday has shown the relation which exists between the amount decomposed and the quantity of electricity passed through solutions. The two laws of Electrolysis discovered by Faraday are :—

Law I. The amount of decomposition is proportional to the quantity of current passed through the decomposed solution.

Law II. The amounts of different elements liberated by the passage of the same quantity of electricity are in the proportion of equivalent weights of these elements.

Thus if the same quantity of current C is passed through (3 voltameters containing) solution of copper sulphate, silver nitrate and through acidulated water and is able to liberate 1 gram of hydrogen then 31.5 gms. of copper, 107.88 grams of silver and 8 grams. of oxygen will be liberated by the same current C . 31.5, 107.88 and 8 are therefore the equivalent weights of copper, silver and oxygen respectively. With the help of this law equivalent weight of a metal can be determined.

(**EXAMPLE 9.** The passage of the same quantity of current through acidulated water and silver nitrate

solution liberates 352 m.l. of oxygen at N. T. P., 6.75 grams of silver and 695 m.l. of hydrogen at N. T. P. Given the equivalent weight of oxygen to be 8, determine the equivalent weights of silver and hydrogen.

Wt. of 1 m.l. Hydrogen at N. T. P. = .00009 gm.

Wt. of 695 m.l. Hydrogen at N. T. P. = .00009 \times 695
= .06255 gm.

Wt. of 352 m.l. Oxygen at N. T. P. = .00009 \times 16
 \times 352 = .505 gm.

.505 gm. Oxygen is liberated by the same current as hydrogen .0625 gm.

8 gms. Oxygen is liberated by the same current as hydrogen = $\frac{.0625 \times 8}{.505} = 1.00$ gm.

\therefore Eq. Wt. of Hydrogen = 1.0.

.505 gm. oxygen is liberated by the same current as 6.75 gms. silver.

\therefore 8 gm. oxygen is liberated by the same current as
= $\frac{6.75 \times 8}{.5} = 108$ gms. silver

\therefore Eq. Wt. of silver = 108. }

EXAMPLE 10. *An electric current is successively passed through voltameter cells containing sulphate solution with copper electrodes and (b) silver nitrate with (a) silver anode and platinum cathode. The increase in weight of the cathodes in cells are .390 gm. and 1.322 gms. of copper and silver respectively. Calculate the equivalent weight of copper that of silver being 108.*

When 1.322 gms. silver is deposited the Cu deposited is .39 gm.

When 108 gms. silver is deposited the Cu deposited is

$$= \frac{.39 \times 108}{1.322} = 31.8.$$

Eq. Wt. of copper = 31.8

OR

$$\frac{\text{Chemical Equivalent of copper}}{\text{Chemical Equivalent of silver}} = \frac{0.39}{1.322}$$

$$\frac{\text{Chemi. Eq. of Cu.}}{108} = \frac{.39}{1.322}$$

$$\therefore \text{Chem. Eq. of Cu.} = \frac{.39 \times 108}{1.322} = 31.8.)$$

Problems.

1. 448 m.l. of hydrogen are evolved at N. T. P. by treating 1.3 gm. of a metal with excess of dilute sulphuric acid. Find the equivalent weight of the metal.

2. If 645 m.l. hydrogen are obtained at N. T. P. by the action of 0.55 gm. of magnesium on excess of hydrochloric acid. What is the equivalent weight of the metal?

3. 0.1178 gm. of a metal dissolved in dilute HCl. evolved 177 m.l. of dry hydrogen at 12° and 766 mm. Find its equivalent weight.

(C. U. 1909.)

4. .25 gram of iron sets free 412 m.l. of hydrogen at 20°C. and 750 mm. pressure from an excess of dilute acid. Calculate the equivalent weight of the metal.

(Aq. tension at 20°C. = 17.5 mm.)

5. 1.05 gm. of a metal gave on oxidation 1.5 gm. of its oxide. What is the equivalent weight of metal?

(P. U. Int. 1925.)

6. 1.95 gms. of a metal were dissolved in nitric acid and the nitrate on being ignited leaves behind 2.43 gms. of the oxide. What is the equivalent weight of the metal?

7. 6.464 gm. of metal were converted into nitrate with nitric acid and ignited. The weight of the oxide is 8.224 gm. Find the equivalent weight of the metal.

8. 3.16 gms. of heated copper oxide were reduced by passing dry hydrogen over it. The weight of water formed is .72 gm. and of copper left is 2.52 gms. Calculate the equivalent weight of copper and oxygen.

9. 2.5 gms. of silver were dissolved in nitric acid and the silver precipitated from it by common salt solution. The precipitate was filtered, dried and weighed to be 3.312 gms. Find the equivalent weight of silver.

(Given eq. wt. Cl = 35.5)

10. 2.452 gms. of silver chloride were reduced on heating in a current of hydrogen to 1.846 gms. of silver. The equivalent weight of silver is 108. Find that of chlorine.

11. 2.16 grams of silver were converted into nitrate with nitric acid and formed 3.76 gms. of silver bromide and adding sodium bromide. Find the equivalent weight of Bromine. (Eq. Wt. Ag = 108).

12. 12.508 gms. of Phosphorous trichloride exactly precipitate 26.978 gms. of silver as silver chloride. Calculate the equivalent weight of Phosphorus. (Eq. Wt. Cl = 35.5, Ag = 107.8)

(Bombay 1912)

13. An electric current is passed through solution of copper sulphate, silver nitrate, nickel ammonium sulphate and acidulated water. What is the amount of copper silver and nickel liberated in each case by the current which sets free 300 m.l. of hydrogen at N. T. P.?

14. The same current was passed through solutions of zinc ammonium oxalate and nickel ammonium sulphate. The weights of zinc and nickel deposited in a certain time were found to be 0.531 gm. and 0.477 gram. If the chemical equivalent of zinc is 32.7, calculate that of Nickel.

(Bombay 1890)

15. An electric Current is passed through solution of copper sulphate and cyanide of silver connected in series. If in a given time 35 gm. of copper is deposited, what will be the weigh of silver deposited in the same time ?
At. wts : Copper = 63.57, Silver = 107.18.

(P. U. 1946)

16. 1.11 grams of the chloride of a metal dissolved in water were treated with an excess silver nitrate solution. The weight of the precipitated silver chloride after washing and drying was found to be 2.87 grams. Calculate equivalent weight of the metal.

(Punjab Inter. 1945)

17. 1.5 gm. of pure carbonate of a metal produce on heating 0.855 gm. of its oxide. Calculate the equivalent weight of the metal.

(Punjab Inter. 1942)

18. Find the equivalent wt. of copper and oxygen from the following data : Dry hydrogen is passed over 1.58 gm. of heated copper oxide producing 0.36 gm. of water and leaving 1.23 gm. of copper after the experiment.

(Allahabad Inter. 1912)

19. If 465 m.l. of hydrogen at N. T. P. are obtained by the action of 0.5 gram of magnesium on excess of hydrochloric acid, what is the equivalent weight of magnesium ?

(U. P. Inter. 1903)

20. On heating in contact with tin, sulphuretted hydrogen (density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur from this.

(Calcutta Inter 1945)

21. The passage of a current of electricity through acidulated water and a solution of copper sulphate liberates 203 m.l. of hydrogen at N. T. P., and deposits 0.571 gm. of copper. Calculate the equivalent weight of copper.

(Punjab B. Sc. 1934)

22. 0.37 gm. of a metal gave on heating in a current of chlorine 1.79 gms of its chloride. Calculate the equivalent weight of the metal.

23. 1.02 gm. of a metal was dissolved in nitric acid and converted into nitrate. The nitrate on strong heating left a residue of oxide weighing 1.2675 gms. of the oxide. Calculate the equivalent weight of the metal.

24. When 0.5 gm. of a metal is dissolved in an acid it gives 183 m.l. of hydrogen at 9°C and 748 m.m. pressure. Find the equivalent weight of the metal.

(Allahbad Inter.)

25. 0.1 gm. of a metal gave on treatment with a dilute mineral acid 34.2 m.l. of hydrogen measured at N. T. P. Calculate the equivalent weight of the metal.

(Calcutta Inter 1935)

26. Iron forms two chlorides containing 34.4% and 44% of Iron. Can you deduce the Eq. wt. of Iron?

(Nagpur Inter. 1935, 27)

27. 2.47 gms. of CuO were obtained by oxidising 1.986 gms. of copper by nitric acid. 0.335 gm. of Cu was precipitated by 0.346 gms. of zinc from CuSO_4 solution.

What are the equivalent weights of copper and zinc ?
(*Patna Inter.*, 1921)

28. 1.0 gm. of KCl solution gives 1.925 gms. of AgCl when treated with excess of AgNO_3 solution. Taking the equivalent weight of Ag as 108 and that of chlorine as 35.5, calculate the eq. wt. of Potassium.

(*U. P. Board Inter.*, (1929)

29. The passage of a current of electricity through acidulated water and solution of copper sulphate liberated 203 m.l. of hydrogen at N. T. P. and desposited 0.571 grams of copper. Calculate the equivalent weight of copper.

(*Calcutta Inter.* 1942; *Delhi* 1934)

30. 1.081 gms. of copper displace 3.670 gms. of silver from a solution of silver nitrate. Find the equivalent weight of copper. [$\text{Ag} = 107.88$]

(*Delhi Preparatory* 1948)

CHAPTER VI

DETERMINATION OF MOLECULAR WEIGHTS

1. Definition. The molecular weight of a substance is defined as the weight of one molecule of the substance as compared with the weight of one atom of oxygen taken as 16 or the wt. of one atom of hydrogen taken as 1.008.

There are several methods of finding the molecular weight of substances but only three important ones are given below :—

METHOD 1. The Vapour Density Method is a very important method for finding the molecular weights of **volatile** substance. In it advantage is taken of **Avogadro's Hypothesis** which states that **equal volumes of all gases under the same conditions of temperature and pressure, contain the same number of molecules.**

The **vapour density (V. D.)** of a substance is the ratio between the weight of a certain volume of its vapour to the weight of the same volume of hydrogen under the same conditions of temperature and pressure.

OR

$$\text{V. D.} = \frac{\text{Wt. of a certain volume of vapour of a substance}}{\text{Wt. of the same volume of hydrogen.}}$$

Let m molecules be present in this volume of vapour of substance.

Then by Avogadro's hypothesis :—

$$\text{V. D.} = \frac{\text{Wt. of } m \text{ molecules of the vapour}}{\text{Wt. of } m \text{ molecules of hydrogen.}}$$

But m is common, therefore,

$$V. D. = \frac{\text{Wt. of one molecule of the substance}}{\text{Wt. of one molecule of hydrogen.}}$$

But the molecule of hydrogen is diatomic, hence its weight is 2.

$$\therefore V. D. = \frac{\text{Wt. of one molecule of the substance}}{2.}$$

But the weight of one molecule of the substance is its molecular weight :—

$$\therefore \text{Molecular weight of the substance} = 2 (V. D.)$$

$$\text{Or Molecular weight} = 2 V. D.$$

Thus molecular weight of a substance can be determined if vapour density of the substance is known.

Determination of Vapour Density.

(1) The most important method of finding vapour density of a substance is **Victor Meyer's Air displacement method**.

The object of this method is to find the volume occupied at N. T. P. by a known weight of the substance on volatilisation. From this volume the weight of the same volume of hydrogen is determined.

In this case a known weight of the substance is vaporised rapidly in a heated Victor Meyer's tube and the air displaced by the vapour is collected over water in a graduated tube. The volume of air displaced is measured under atmospheric temperature and pressure. This volume is then determined at N. T. P. and then the weight of the same volume of hydrogen is found out.

EXAMPLE 1. 2308 gms. of a volatile substance were vaporised in a Victor Meyer's apparatus and the air displaced was 46.4 m.l. collected over water at 18°C. and 772 mm. pressure. Aqueous Vapour tension at 18°C. = 15.4 mm. Determine the molecular weight of the substance.

$$P = 772 - 15.4 = 756.6 \text{ mm.}$$

$$P_0 = 760 \text{ mm.}$$

$$V = 46.4 \text{ m.l.}$$

$$V_0 = ?$$

$$T = 273 + 18 = 291 \text{ A.}$$

$$T_0 = 273.$$

$$\text{Since } \frac{P_0 V_0}{T_0} = \frac{PV}{T}$$

$$\therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\text{Or } V_0 = \frac{46.4 \times 756.6 \times 273}{291 \times 760} = 43.3 \text{ m.l.}$$

1 m.l. of hydrogen at N. T. P. weighs .00009 gm.

$$\therefore 43.3 \text{ m.l. of hydrogen at N. T. P. weighs} = 43.3 \times .00009 \\ = 0.0039 \text{ gm.}$$

V. D. of the substance

$$= \frac{\text{Wt. of } 43.3 \text{ m.l. of vapour of the subs. at N. T. P.}}{\text{Wt. of } 43.3 \text{ m.l. of hydrogen at N. T. P.}} \\ = \frac{.2308}{.0039} = 59.2.$$

$$\text{Hence Mol. Wt.} = 2 \times 59.2 = 118.4.$$

EXAMPLE 2. 0.232 gm of a volatile substance displaced 37.5 m.l. of moist air at 11°C. and 752 mm. pressure. Calculate the molecular weight of the substance. (Aq. Tension at 11°C = 9 mm.

(P. U. 1948)

$$P = 752 - 9 = 743 \text{ mm.}$$

$$P_0 = 760 \text{ mm.}$$

$$V = 37.5 \text{ m.l.}$$

$$V_0 = ?$$

$$T = 273 + 11 = 284$$

$$T_0 = 273$$

$$\text{Since } \frac{P_0 V_0}{T_0} = \frac{PV}{T}$$

$$\therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\text{Or } V_0 = \frac{37.5 \times 273 \times 743}{760 \times 284} = 35.25 \text{ m.l.}$$

1 m.l. of hydrogen at N. T. P. weighs .00009 gm.

$$35.25 \text{ m.l. } \therefore .00009 \times 35.25 \\ = 0.0032 \text{ gm.}$$

V. D. of the substance.

$$= \frac{\text{Wt. of 35.25 m.l. of vapour at N. T. P.}}{\text{Wt. of 35.25 m.l. of hydrogen at N. T. P.}}$$

$$= \frac{.2320}{.0032} = 72.5$$

Hence Molecule Wt. $= 2 \times 72.5 = 145$

(ii) The vapour density of gases can also be determined by the diffusion method by the application of Graham's Law of diffusion of gases. (Chapter III Article 5)

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$$

This method is used for the determination of Molecular weights of gases. The gas whose molecular weight is to be determined is allowed to diffuse through a porous vessel and its rate of diffusion compared with that of a gas whose mole. wt. is known. Then by Graham's Law we have

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Knowing r_1 , r_2 and M_1 , we can calculate M_2 .

EXAMPLE 3. *The relative rates of diffusion of a gas as compared with that of carbon dioxide is as 266 : 218. Calculate the Mole. wt. of the gas.*

(U. P. Board, Inter, 1940)

Let M be the molecular wt. of the gas.

Mole. wt. of $\text{CO}_2 = 44$

$$\therefore \frac{266}{218} = \sqrt{\frac{44}{M}}$$

$$\text{Or } \frac{44}{M} = \left(\frac{266}{218} \right)^2$$

$$\text{Or } M = 44 \times \left(\frac{218}{266} \right)^2 = 29.56$$

EXAMPLE 4. 180 m.l. of a hydrocarbon diffuse in 15 minutes while under similar condition 120 m.l. of sulphur dioxide diffuse in 20 minutes. If the mole. wt. of sulphur dioxide is 64, what is the mole. wt. of the hydrocarbon.

Time for diffusion of 120 m.l. of sulphur dioxide = 20 minutes.

$$\therefore \text{Time for diffusion of 180 m.l. of sulphur dioxide} \\ = 20 \times \frac{180}{120} = 30 \text{ minutes}$$

And the time taken for diffusion of 180 m.l. of hydrocarbon = 15 minutes

Therefore if M is the Mole wt. of the hydrocarbon, then,

$$\frac{15}{30} = \sqrt{\frac{M}{64}}$$

$$\text{Or } \frac{M}{64} = \left(\frac{15}{30} \right)^2 = \frac{1}{4}$$

$$M = 16.$$

\therefore Mole. wt. of the hydrocarbon = 16.

METHOD II. Gram Molecular Volume Method :—

It is based on the fact that gram molecule of any gas at N.T.P. will occupy a volume equal to 22.4 litres.

To calculate the molecular weight, the weight of a certain volume of a gas under known conditions of temp. and pressure is determined, the volume is converted to N.T.P. with the help of gas equation, and then the weight of 22.4 litres of the gas at N.T.P. is calculated. This gives the Mole. wt. of the gas.

EXAMPLE 5. 2.83 gms of a gas occupy 3.895 litres

at 20°C and 780 mm. pressure. Calculate the Molecular weight.

(P. U. 1940)

$$P=780$$

$$V=3.895$$

$$T=273+20=293$$

$$P_0=760$$

$$V_0=?$$

$$T_0=273$$

$$\frac{PV}{T} = \frac{P_0 V_0}{T_0}$$

$$\therefore V_0 = \frac{PV}{T} \times \frac{T_0}{P_0}$$

$$\therefore V_0 = \frac{780 \times 3.895 \times 273}{293 \times 760} = 3.717$$

Weight of 3.717 litres at N.T.P. = 2.83 gms.

$$\text{,, ,, 22.4 ,, ,, ,,} = \frac{2.83 \times 22.4}{3.717}$$

$$= 17.05 \text{ gms.}$$

\therefore Mole. wt. of the substance = 17.05

Problems.

1. ✓ 0.108 gms. of a liquid were subject to Victor Meyer's treatment and displaced 20 m.l. of air at 16.5°C. and 740 mm. pressure. Find the Molecular weight of the substance. (Aq. tension 16.5°C. = 15 mm.)

2. In Victor Meyer's apparatus 0.2501 gm. of a substance were vaporised and 52 m.l. of air were collected at 20°C. and 757.5 mm. pressure. Calculate the molecular weight of the substance.

3. In a Victor Meyer's determination of the vapour density 0.0926 gms. of a liquid gave 28.9 m.l. of gas collected over water at 16°C. and 753.6 mm. pressure. Calculate the vapour density of the liquid.

(Aq. tension at 16°C. = 13.5 mm.)

4. ✓ The rates of diffusion of CO_2 and ozone are in the ratio of 0.29 to 0.271. The Mole. wt. of carbon dioxide is 44. What is the Mole. wt. of ozone?

5. ✓ If 50 volumes of hydrogen take 85 seconds to diffuse from a vessel, how long will it take 35 volumes of nitrous oxide to do so under the same conditions.

6. ✓ The rates of diffusion of two gases A and B are in the ratio 5 : 6. The Mole. wt. of B is 28, find that of A.

7. ✓ The relative rate of diffusion of a gas as compared with carbon dioxide is as 27 : 29. Calculate the relative density of the gas, that of carbon dioxide being 22.

8. ✓ Calculate the molecular weight of an unknown gas which under precisely similar conditions takes 1.117 times as long as oxygen to diffuse through an aperture.

9. ✓ 45 gm. of chloroform displaced 91.5 m.l. of air measured over water at 22°C. and 755 mm. pressure. Calculate the vapour density and mole. wt. of the substance. (Aq. Tension at 22°C = 20 mm.)

10. A vapour density determination by Victor Meyer's method gave the following result; 0.1 gm of the substance displaced 27 m.l. of air measured at 15°C. and 745 mm. pressure (vapour tension at 15°C = 12.7 mm.) Determine the molecular weight.

(P. U. 1937)

11. ✓ 0.220 gms. of a substance when vaporised, displaced 45 m.l. of air measured over water at 20°C and 755 mm. pressure. Calculate the mole. wt. of the substance. (Tension of aqueous vapour at 20°C = 17.4 mm. one m.l. of hydrogen at N. T. P. weighs 0.00009 gm.)

(P. U. 1945)

12. ✓ In a determination of molecular weight by Regnault's methods 372.46 m.l. of the gas at N. T. P. were found to weigh 0.283 gms. Calculate the molecular weight.

13. The molecular weight of oxygen is 32. Calculate the weight of 260 m.l. of the gas measured at 27°C . and 750 m.m. pressure.

14. 22 m.l. of moist air was collected at 16.5°C and 707.5 mm. pressure when 0.1003 gms of a substance was vaporised in Victor Meyer's apparatus. Calculate the molecular weight of the substance. (Aq. tension at $16.5^{\circ}\text{C} = 13.5$ mm)

(P. U. 1943)

15. In determination of the molecular weight of a substance by Victor Meyer's method 0.1630 gms. of substance gave 40.4 m.l. of vapour at 20°C and 740 mm. pressure. Find the molecular weight of the substance.

16. 0.0623 gms. of a substance gave by Victor Meyer's method 31.5 m.l. of moist air measured at 15°C and 750 mm. Find the molecular weight of the substance. (Tension of aqueous vapour at $15^{\circ} = 12.7$ mm.)

17. A quantity of gas weighing 0.062 gm. occupies 25.64 m.l. at 100°C and 741 m.m. pressure. Calculate the molecular weight of the gas.

18. In a Victor Meyer determination, 0.0926 gms. of a liquid gave 28.9 m.l. of gas collected over water and measured at 16°C and 753.6 m.m. pressure. Calculate the vapour density and the molecular weight of the substance. (Aq Tension at $16^{\circ}\text{C} = 13.6$ mm.)

19. 0.3 gms. of a volatile organic substance when vaporised in a Victor Meyer's apparatus displaced 93.0 m.l. of air measured over water at 16°C and 771 mm. pressure. Calculate the vapour density and molecular weight of the substance. (Aqueous tension at $16^{\circ}\text{C} = 13.5$ mm.) [Given that 1 m.l. of hydrogen at N.T.P. weighs 0.00009 gms,]

20. 0.6 gram of a volatile substance displaced 123 m.l. of moist air at 20°C and 757.4 mm. pressure. Cal-

calculate the molecular weight of substance. (Aq. tension at $16^{\circ}\text{C} = 13.5 \text{ mm.}$)

(P. U. 1932)

21. 0.1680 gm. of a substance when vaporised displaced 49.4 m.l. of air at 20°C and 740 mm. pressure. Calculate the vapour density and molecular weight of the substance. (Aq. tension at 20°C is 18 mm. and one m.l. of hydrogen at N.T.P. weigh 0.00009 gm.)

(U. P. Board Inter 1945)

CHAPTER VII

DETERMINATION OF ATOMIC WEIGHTS

Definition. The atomic weight of an element is the "average" relative weight of its atom compared with the weight of an oxygen atom taken as 16.

On this standard atomic weight of hydrogen comes out to be 1.008.

The use of the word 'average' in the above definition refers to the fact that the different atoms of an element though having identical chemical behaviour, may have different masses. Such atoms of an element are called *isotopes*. Now as the proportion of different *isotopes* in an element is always constant, the average atomic weight of the element will be also constant.

Determination of atomic weight. The finding of exact atomic weights of elements is of fundamental importance in Chemistry. The common methods used for finding atomic weights are discussed below :—

METHOD I. This method is based on the hypothesis that an atom is the smallest particle of an element that can take part in a chemical reaction. **The atomic weight of an element is, therefore, the smallest weight of the element present in the molecular weight of any of its compounds.** In view of this, the atomic weight of an element can be found out by carrying an exact analysis of as many compounds of the element as possible and then determination of their molecular weights. The weights of the element present in one molecule of the various compounds are then determined. The smallest of these weights is most probably the atomic weight of the element.

EXAMPLE 1. *The following compounds of sulphur are analysed and their vapour densities or molecular weights determined. The results are given below. Find out the approximate atomic weight of sulphur.*

Name of Compound.	V. D.	Percent Sulphur in the Compound.
1. Sulphur dioxide	32.1	50
2. Sulphur trioxide	40.03	40
3. Sulphuretted hydrogen	17.03	94.1.
4. Carbon bisulphide	38.04	84.2
	Mol. Wt.	
5. Copper sulphate	250	12.8
6. Ferrous sulphate	278	11.51.
7. Magnesium sulphate	246	13.01.

Mol. wts. of above Compounds are 64.2, 80.06, 34.06, 76.08, 250, 278 and 246 respectively.

Weights of sulphur in one molecular weight of these Compounds are :—

$$(1) 64.2 \times \frac{50}{100} = 32.1$$

$$(5) 250 \times \frac{12.8}{100} = 32.0.$$

$$(2) 80.06 \times \frac{40}{100} = 32.02.$$

$$(6) 278 \times \frac{11.51}{100} = 32.00.$$

$$(3) 34.06 \times \frac{94.1}{100} = 32.02.$$

$$(7) 246 \times \frac{13.01}{100} = 32.04.$$

$$(4) 76.08 \times \frac{84.2}{100} = 64.04$$

Thus the smallest weight of sulphur contained in molecular weight of any of the above compounds is 32. The approximate atomic weight of sulphur, therefore, is 32.

METHOD II. In this method advantage is taken of the relationship between atomic weight, equivalent weight and Valency.

At. Wt. = Equivalent Weight \times Valency. Valency is defined to be the number of hydrogen atoms with which one atom of an element combines.

Valency is always a whole number because atom is the smallest portion that takes part in a reaction and is chemically indivisible. If valency of an element is known and its equivalent weight is determined, then the atomic weight can easily be calculated.

EXAMPLE 2. *1.769 gms. of pure copper were dissolved in nitric acid, and the solution is evaporated to dryness. The residue is ignited and the weight of the cupric oxide CuO obtained was found to be 2.214 gms. Find the atomic wt. of copper.*

Wt. of oxide of copper = 2.214 gms.

Wt. of pure copper = 1.769 gms.

\therefore Wt. of oxygen = .445 gm.

.445 gm. oxygen combines with copper 1.769 gms.

\therefore 8 gm combines with copper = $\frac{1.769 \times 8}{.445}$
= 31.8.

\therefore Eq. Wt. of Cu = 31.8.

Since in CuO one atom of divalent oxygen has combined with one atom of copper, therefore copper is divalent.

\therefore **At. Wt. of Cu**, = $2 \times 31.8 = 63.6$.

METHOD III. Dulong and Petit's Method. Dulong and Petit have found that the product of the atomic weight of an element and its specific heat in the solid state is constant and is approximately equal to 6.4. It is called **Atomic Heat**.

Or At. Wt. \times Sp. Ht. = **Atomic Heat** = 6.4.

\therefore At. W. = $\frac{6.4}{\text{Sp. Ht.}}$

Therefore the specific heat of an element can be used for calculating its approximate atomic weight, which is then used for getting the exact valency of the element according to the equation, $\text{Valency} = \frac{\text{At. Wt. (approximate)}}{\text{Eq. Wt.}}$

As the atomic weight so obtained is approximate, the valency obtained is not a whole number, but, as the valency, must always be a whole number, it is made to the nearest whole number. The exact valency of the element having thus been obtained, the relationship, $\text{At. Wt.} = \text{Eq. Wt.} \times \text{valency}$, is then applied for determining the exact atomic weight.

EXAMPLE 3. *1.02 gms. of a metal formed 1.31 gms of its oxide. The specific heat of the metal is .056. Find the exact Atomic weight of the metal.*

Wt. of oxide = 1.31, Wt. of metal = 1.032.

\therefore Wt. of oxygen = .278 gm.

.278 gm. oxygen combines with 1.032 gms metal.

\therefore 8 gms. " " " " metal = $\frac{1.032 \times 8}{2.78}$

$$= \frac{8.256}{2.78} = 29.7 \text{ gms}$$

\therefore The equivalent Wt. of the metal = 29.7.

Now approximate At. Wt. = $\frac{6.4}{.056} = 114.3$.

(Dulong and Petit's Law)

\therefore Valency = $\frac{114.3}{29.7} = 3.9$.

The valency is therefore equal to 4 i. e., the nearest whole number.

Hence exact atomic weight of the metal

$$= 29.7 \times 4 = 118.8.$$

METHOD IV. **Mitscherlich's Law of Isomorphism** states that "Truly Isomorphous substances have similar chemical constitution." This means that the same number of atoms combined in the same way give rise to the same crystalline form. The similarity in crystalline structure is very useful in fixing the atomic weights as is clear from the following examples.

EXAMPLE 4. 1.112 gms. of aluminium forms 2.102 gms. of oxide. The sulphate of aluminium forms a double salt with potassium sulphate, which is isomorphous with chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$. The valency of chromium is 3. What is the exact atomic weight of aluminium?

Wt. of oxide = 2.102 gm.

Wt. of Al. = 1.112 gms.

\therefore oxygen = .99 gm.

.99 gm. oxygen combines with 1.112 gms. Al.

$$\begin{aligned} \therefore 8 \text{ gms. oxygen combines with} &= \frac{1.112 \times 8}{.99} \\ &= \frac{8.896}{.99} = 8.98 \end{aligned}$$

Eq. Wt. Al. = 8.98.

Since the double salt potassium aluminium sulphate is isomorphous with chrome alum, the valency of aluminium like that of chromium, must be 3.

\therefore At. Wt. of Al. = $8.98 \times 3 = 26.94$.

EXAMPLE 5. Potassium sulphate and selenate are isomorphous. The percentage of sulphur is 18.39 in the sulphate and 45.42% selenium in the same weight of selenate. Atomic weight of sulphur is 32. Find that of selenium.

$$\frac{\text{At. Wt. of selenium}}{\text{At. Wt. of sulphur}} = \frac{45.42}{18.39}$$

$$\therefore \text{At. Wt. of selenium} = \frac{45.42}{18.39} \times 32 = 79$$

EXAMPLE 6. 5 gms. of a metallic bromide gave 7.2552 gms. of iodide. What would be the atomic weight of the metal if it were univalent, bivalent and trivalent?

(At. Wt. Bromine = 79.95 and iodine = 126.85).

(P. U. Int. 1929)

Suppose the atomic weight of the metal = x .

(a) **The metal is univalent.**

The formula weight of the bromide = $x + 79.95$.

The formula weight of iodide = $x + 126.85$.

$$\therefore \frac{\text{Formula weight of the bromide}}{\text{Formula weight of the iodide}} = \frac{x + 79.95}{x + 126.85} = \frac{5}{7.2552}$$

Or By simplification $x = 24.1$ is At. Wt. if x is univalent.

(b) **If the metal is divalent.**

The formula weight of the bromide = $x + 2 \times 79.95$
 $= x + 159.90$.

The formula weight of the iodide = $x + 2 \times 126.85$
 $= x + 253.70$

$$\therefore \frac{\text{Formula Wt. of bromide}}{\text{Formula Wt. of iodide}} = \frac{x + 159.9}{x + 253.7} = \frac{5}{7.2552}$$

By simplification $x = 48.1$ is the At. Wt. if metal is divalent.

(c) **If the metal is trivalent.**

The Formula weight of the bromide = $x + 3 \times 79.95$
 $= x + 239.85$

The Formula weight of the iodide = $x + 3 \times 126.85$
 $= x + 380.55$.

$$\therefore \frac{\text{Formula Wt. of the bromide}}{\text{Formula Wt. of the iodide}} = \frac{x+239.85}{x+380.55}$$

By simplification $x=72.1$ is the At. Wt. if x is trivalent.

EXAMPLE 7. 1.5 of pure carbonate of a divalent metal produce on heating 0.855 gms. of its oxide. Calculate the weight of the metal.

(P. U. 1942)

Let the At. Wt. of the metal be M

Then Mole. Wt. of carbonate (MCO_3) = $M+12+3 \times 4$
 $= M+60$

Mole. Wt. of oxide (Mo) = $M+16$.

Since $\frac{\text{Mole. Wt. of carbonate}}{\text{Mole. Wt. of oxide}}$

$$= \frac{\text{Wt. of carbonate}}{\text{Wt. of oxide}}$$

$$\therefore \frac{M+60}{M+16} = \frac{1.5}{0.855}$$

$$\text{Or } 0.855 M + 60 \times 0.855 = 1.5 M + 1.5 \times 16$$

$$\text{Or } 0.645 M = 27.3$$

$$M = 42.3. \text{ Ans.}$$

EXAMPLE 8. The oxide of an element contains 33.3% of the element. The same element forms a chloride whose vapour density is 59.50. Calculate the valency, the Equivalent weight and the atomic weight of the element.

(P. U. 1941, 48)

(a) Let the element be M .

$$M \text{ in the oxide} = 33.3\%$$

$$\therefore \text{oxygen in the oxide} = 100 - 33.3 = 66.7\%$$

66.7 parts by weight of oxygen combine with 33.3 parts of M

$\therefore 8$ " " " " " " " " with

$$\frac{33.3}{66.7} \times 8 = 4 \text{ parts of element}$$

Hence Eq. Wt. of element is = 4.

(b) Let the valency of the element be V

Since chlorine is monovalent,

\therefore the formula of the chloride is MCl_V

\therefore Mole. Wt. of $MCl_V = \text{At. Wt. of } M + V + 35.5$

$$= V \times \text{Eq. Wt. of } M + V \times 35.5$$

$$= V \times 4 + V \times 35.5$$

$$= 39.5 \times V$$

But Mole. Wt. = $2 \times V \cdot D = 2 \times 59.25 = 118.5$

$$\therefore 39.5 \times V = 118.5 \quad \text{Or } V = 3$$

\therefore Valency of the metal = 3.

(c) At. Wt. = Eq. Wt. \times Valency

$$= 4 \times 3 = 12 \text{ Ans.}$$

EXAMPLE 9. *The chloride of a trivalent metal contains 40.5% of chlorine. Find the atomic weight of the element.*

(P. U. 1940)

The chloride contains 40.5% of the chlorine

\therefore " " " (100 - 40.5) = 59.5% of the element

Now 40.5 chlorine is contained with 59.5 of the metal

$$\therefore 35.5 \quad " \quad " \quad " \quad " \quad \frac{59.5}{40.5} \times 35.5$$

$$= 52.14 \text{ of the metal}$$

\therefore Eq. Wt. of the metal = 52.14

And At. Wt. of the metal = $52.14 \times 3 = 156.42$. Ans
 (as the metal is trivalent)

Problems

1. The percentage amount of nitrogen and the vapour density of the following compounds were determined and are given below :—

Compound	V. D.	% Nitrogen
1. Ammonia	8.5	82.4
2. Methyl Amine	15.5	45.2
3. Nitrous oxide	22	63.6
4. Ethyl Nitrate	45.5	63.6
5. Cyanogen	26	53.8
6. Nitric oxide	15	46.7

Calculate the At. wt. of Nitrogen

2. The percentage of carbon in the following compounds and their molecular weights are given below :—

Compound	Mol. Wt.	Percent carbon in the Compound
Benzene	78	92.31.
Methane	16	75.0
Ethylene	28	85.7.
Carbon monoxide	28	42.65.
Carbon dioxide	44	27.27.
Carbon disulphide	76	15.8.
Propylene	42	85.7

Calculate the atomic weight of Carbon.

3. The molecular weights of the following compounds and the percentage of oxygen in them are given below :—

Calculate the atomic weight of oxygen.

Compound.	Mol. Wt.	Percent Oxygen in the Compound.
Carbon dioxide	44	72.73.
Sulphur dioxide	64	50.
Nitrous oxide	44	36.4.

Carbon monoxide	28	57.15.
P_2O_5	142	56.2

4. The specific heat of a metal is .24 and .18 gm. of it combines with .16 gm. of oxygen. Find the atomic weight of the metal.

(P. U. 1913)

5. The specific heat of Indium is .057, of lead is .0315 and of iron is .114. What are the atomic weights of the metals.

6. A metallic chloride contains 26.2 percent of chlorine and vapour density of the metal is 101.7, specific heat is .033. Calculate equivalent weight, atomic weight, and molecular weight of the metal. (Cl.=35.5)

(P. U. 1924)

7. .25 gm. of a metal gave 233 m.l's of hydrogen at N. T. P. on treatment with an acid. If specific heat of metal is .245. Calculate atomic weight of the metal.

(P. U. 1926)

8. Dolomite and magnesite are isomorphous compounds and the percentage of magnesium in the latter is 28.6. Determine the equivalent weight of magnesium.

9. Potassium chlorate is isomorphous with potassium permanganate. The percentage of chlorine in former is 25.59 and of manganese in the latter 34.76. If the atomic weight of manganese is 54.95. Find the atomic weight of chlorine.

10. On dissolving .444 gm. of a metal in dil. sulphuric acid 177 m.l. of hydrogen at 10°C. and 750 mm. are liberated. The specific heat of the metal is .107. What is the exact atomic weight of the metal?

(P. U. 1928 Dec)

11. Potassium sulphate is isomorphous with potass-

ium chromate which contain 26.78% of chromium. Find the atomic weight of chromium.

12. One gram of the chloride of a metal, when treated with excess of silver nitrate, formed .965 gm. of Ag. Cl. Calculate the atomic weight of the metal, given that it closely resembles Barium in its properties.

(P. U. 1932)

13. The percentage of phosphorus in the following compounds with their vapour densities are given.— Calculate the atomic weight of Phosphrus.

Compound	V. D.	% of P.
Phosphorus trichloride	70	22.5.
trioxide	110	56.4.
pentachloride	104.25	14.8.
pentaoxide	150	43.7.
penta sulphide	111	27.9.

14. The chloride of a metal was found on analysis to contain 48.6 gms. of metal for 35.5 gms. of chlorine. The specific heat of the metal is .0324. Find the atomic weight of the metal.

(P. U. 1925)

15. Gallium forms a potash alum isomorphous with ordinary potash alum with fomula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$. The percentage of gallium in the alum is 13.52. Calculate the atomic weight of gallium.

16. The percentage of zinc in calamine is 52. If calamine forms isomophous crystals with magnesite whose formula is $Mg CO_3$, calculate the atomic weight of zinc.

17. The oxide of an element contains 28.6% of oxygen and the vapour density of its chloride is 55.5. Calculate (a) the atomic weight. (b) the Eq. Wt. (c) the valency of the element.

(P. U. 1944)

18. 2.380 gms. of tin, on treatment with conc. HNO_3 and subsequent ignition gave 3.022 gms. of the oxide. The specific heat of the metal is 0.055. Calculate the exact atomic weight of tin.

19. 0.18 gm. of an element combines with 0.16 gm. of oxygen. Its specific heat is 0.24. Find the atomic weight, equivalent weight and valency.

(P. U. 1925)

20. On dissolving 0.444 gm. of a metal in dilute sulphuric acid 177 m.l. of hydrogen at 10°C . and 750 mm pressure were obtained. The specific heat of the metal was 0.107. Calculate its exact atomic weight.

(P. U. 1928)

21. The chloride of a metal was found on analysis to contain 79.77% of chlorine. The specific heat of the metal was 0.237. Calculate the exact atomic weight of the metal,

(U. P. Inter Board 1941)

22. The vapour density of the metallic chloride in the vapourous state is 66.8. One gm. of the chloride with excess of silver nitrate gave 3.225 gm of Silver chloride. Calculate the atomic weight of the metal.

(U. P. Inter Board 1935)

23. The chloride of a metal was found to possess a vapour density of 66.6 ($\text{H}=1$) and contained 79.8% of chlorine. Calculate the atomic weight and valency of the metal.

24. 0.5395 gm. of a metal when converted into its chloride, weighs 0.7175 gm. The sp. heat of the metal is 0.059. What is its correct atomic weight?

(Bombay Inter 1915)

25. 1.0 gm. of a metal gave on treatment with a

dilute mineral acid 1242 ml. of hydrogen at N. T. P. Calculate the equivalent weight of the metal, also its atomic weight, if the specific heat is 0.238.

(*U. P. Inter Board 1932*)

26. The oxide of an element contains 53% of the element and the vapour density of its chloride is 66. Calculate (a) At. Wt. (b) Valency.

27. The chloride of a metal was found on analysis to contain 48.6 gms. of the metal per 35.5 gms. of Chlorine. The specific heat of the metal is 0.0324. Find the atomic weight of the metal.

(*P. U. 1915*)

28. The chloride of an element contains 58.68% chlorine. The vapour of the chloride is 91 times as heavy as an equal volume of hydrogen at N. T. P. Find the equivalent weight, atomic weight and valency of the element.

(*Punjab B. Sc., 1917*)

29. The chloride of a metal was found to contain 47.22% gms. of the metal. Its specific heat is 0.0104. What is the exact atomic weight?

(*Bombay Inter 1934*)

30. 0.148 gm. of a metal on treatment with dilute hydrochloric acid evolved 152 ml. of moist hydrogen at 17°C and 740 m.m. pressure. The specific heat of the metal is 0.25. Calculate its equivalent weight, atomic weight and valency. (Aqueous tension at 17°C is 15 m.m.)

(*Delhi Preparatory 1946*)

31. An oxide of a metal contains 30% of oxygen, its chloride contains 65.5% of chlorine. 100 ml. of the vapour of the chloride at N. T. P. weigh 0.72 gm. The specific heat of the metal is 0.114. What are its eq. wt., at. wt.

(*Patna Inter 1937*)

32. A metallic oxide was found to contain 52.94% of metal and 47.06 of oxygen. A rapid determination of the specific heat of the metal gave 0.25. What is the exact atomic weight of the metal ($O=16$).

(U. P. Board Inter 1936)

33. 0.75 gm. of the chloride of a metal when treated with excess of silver nitrate produced 1.354 gm. of dry AgCl. Calculate the atomic weight of the metal, given that it closely resembles Barium in its properties.

(Delhi Inter 1973)

CHAPTER VIII

DETERMINATION OF PERCENTAGE COMPOSITION OF DIFFERENT COMPOUNDS.

The percentage composition of an element in a chemical compound is the relative weight of the element present in 100 parts of the compound.

The percentage composition of different elements is calculated from the formula of the compound.

If the formula of a compound is known, we can calculate the molecular weight by adding up the weights of atoms of each element present in the molecule.

For the determination of the percentage of each element present in the compound, we have to calculate the weight of the element that would be present in 100 gms. of the compound, from the fact that we know the weight of each element present in the gram molecule of the substance.

EXAMPLE 1. *Calculate the percentage composition of sulphuric acid, H_2SO_4 .*

Now from the formula H_2SO_4 we find that the molecular weight will be $(2 \times 1) + 32 + 16 \times 4$.

$$= 2 + 32 + 64 = 98.$$

So that 98 grams of sulphuric acid contain

2gms of hydrogen,
32 gms. of sulphur and
64 gms. of oxygen.

$$\therefore \text{percentage of hydrogen in the acid} = \frac{2 \times 100}{98} \\ = 2.04.$$

$$\% \text{ age of sulphur in the acid} = \frac{32 \times 100}{98} = 32.65.$$

$$\text{and } \% \text{ age of oxygen in the acid} = \frac{64 \times 100}{98} = \frac{65.31}{100}$$

EXAMPLE 2. *The formula of potassium ferrocyanide is $K_4Fe(CN)_6$. Calculate the percentage of nitrogen in the compound.*

The formula of the compound = $K_4Fe(CN)_6$.

The weight of different elements in the molecule

$$= 4K = 39 \times 4 = 156$$

$$Fe = 56$$

$$6C = 12 \times 6 = 72$$

$$6N = 14 \times 6 = 84$$

\therefore The molecular weight = 368.

So that 368 gms. of the compound contain 84 gms. of nitrogen.

$$\therefore \text{percentage of nitrogen} = \frac{100 \times 84}{368} = 22.89.$$

b. In case the Compound contains water of Crystallisation, it is always calculated as such and not as oxygen and hydrogen separately.

EXAMPLE 3. *Calculate the percentage composition of ferrous sulphate. $FeSO_4 \cdot 7H_2O$.*

$$Fe = 56$$

$$S = 32$$

$$4O = 16 \times 4 = 64.$$

$$7H_2O = 18 \times 7 = 126.$$

\therefore The molecular weight = 278.

Hence 278 gms. of the salt contain.

$$56 \text{ gms. of iron } \therefore \% \text{ age of iron} = \frac{56 \times 100}{278} = 20.14.$$

$$32 \text{ gms. of sulphur } \therefore \% \text{ age of sulphur} = \frac{32 \times 100}{278} = 11.51.$$

$$64 \text{ gms. of oxygen } \therefore \% \text{ age of oxygen} = \frac{64 \times 100}{278} = 23.03.$$

$$\begin{aligned} \text{and 126 gms. of water } \therefore \% \text{ age of water} &= \frac{126 \times 100}{278} \\ &\text{(of crystallisation)} \quad = 45.32. \\ &\quad \quad \quad \underline{100.00.} \end{aligned}$$

c. In certain cases the percentages of the different elements are represented in the form of their oxides. For example sodium carbonate is represented as a combination of sodium oxide (Na_2O) and carbon dioxide (CO_2).

Similarly calcium silicate CaSiO_3 is represented as a combination of calcium oxide and silicate SiO_2 .

EXAMPLE 4. Calculate the percentage of calcium oxide and silica in calcium silicate, CaSiO_3 .

Now CaSiO_3 is $\text{CaO} + \text{SiO}_2$.

\therefore The weight of CaO in the molecule

$$= 40 + 16 = 56$$

and the weight of SiO_2 in molecule

$$= 28 + 32 = 60$$

and the molecular weight

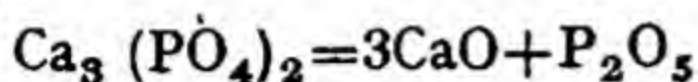
$$= 56 + 60 = 116.$$

$$\therefore \% \text{ age of CaO in the compound} = \frac{56 \times 100}{116} = 48.27.$$

$$\begin{aligned} \text{and the percentage of SiO}_2 \quad \text{''} \quad \text{''} &= \frac{60 \times 100}{116} \\ &= 51.73. \end{aligned}$$

EXAMPLE 5. Calculate the percentage of phosphorus pentoxide in calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$.

Calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ may be represented as the combination of the oxides of calcium and phosphorus, thus—



$$3\text{CaO} = 3 \times (40 + 16) = 3 \times 56 = 168$$

$$\text{P}_2\text{O}_5 = 31 \times 2 + 16 \times 5 = 62 + 80 = 142$$

$$\text{Mole. wt. of the compound} = 168 + 142 = 310$$

$$\text{Wt. of } \text{P}_2\text{O}_5 \text{ in 310 gms. of } \text{Ca}_3(\text{PO}_4)_2 = 142 \text{ gms.}$$

$$\therefore \% \text{age of } \text{P}_2\text{O}_5 \text{ in the compound} = \frac{142 \times 100}{310} = 45.8$$

Problems

1. Find the percentage composition of each of the following compounds :—

[a] Potassium Chloride, KClO_3 .

[b] Ferric Oxide, Fe_2O_3 .

[c] Copper Sulphate, $\text{Cu}_4\text{SO}_4 \cdot 5\text{H}_2\text{O}$.

[d] Nitric Acid, HNO_3 .

[e] Magnissium Sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

[f] Ferrous Sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

[g] Aluminium Oxide, Al_2O_3 .

[h] Potassium Ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$

2. What is the percentage of oxygen in the following compounds.

[a] FeSO_4 .

[b] $\text{K}_2\text{Cr}_2\text{O}_7$

[c] $\text{C}_6\text{H}_{12}\text{O}_6$

[d] Fe_2O_3

[e] HNO_3

[f] Al_2O_3

3. Find the percentage of Na_2O , CO_2 , H_2O in sodium carbonate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

4. Calculate the percentage of nitrogen in sodium nitrate and potassium nitrate.

5. Determine the percentage composition of the following compounds:—

[a] Chalk, CaCO_3

[b] Mohr's salt, $\text{Fe SO}_4 (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$

[c] White vitriol. $3 \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

[d] Lead nitrate $\text{Pb} (\text{NO}_3)_2$

[e] Magnesium Chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[f] $\text{KAl Si}_3 \text{O}_8$

[g] Sodium Thiosulphate, $\text{Na}_2 \text{S}_2 \text{O}_3$

[h] Barium Chloride, $\text{Ba Cl}_2 \cdot 2\text{H}_2\text{O}$

6. Copper sulphate crystals. $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$ lose the whole of their water of crystallisation on heating. Calculate the percentage loss in weight that will take place on heating a sample of the crystals.

7. Washing soda, $\text{Na}_2 \text{CO}_3 \cdot 10\text{H}_2\text{O}$ loses its water of crystallisation on standing due to efflorescence. Calculate the percentage loss in weight that washing soda undergoes on standing.

CHAPTER IX

DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULAE OF COMPOUNDS.

Determination of Empirical Formulae. The empirical formula of a compound is the simplest expression which represents the relative number of atoms of each element present in a molecule of the substance. The empirical formula of water is H_2O , the same as the chemical formula but in case of hydrogen peroxide the empirical formula is HO while the actual formula is H_2O_2 . Thus the empirical formula may be the same as, or a submultiple of, the actual formula of the compound.

The empirical formula can be calculated from the percentage composition in the following way :—

(i) Divide the percentage of each element by its atomic weight.

(ii) Divide the quotients so obtained by the lowest among them. The nearest whole number in each case represents the relative number of atoms of each element in the empirical formula.

EXAMPLE 1. The percentage composition of a compound is given below. Find its empirical formula.

$K=31.8\%$, $O=39.2\%$, and $Cl=29\%$

Dividing the percentage of each element by its atomic weight, we have :—

$$K = \frac{31.8}{39} = .833, \quad O = \frac{39.2}{16} = 2.45, \quad Cl = \frac{29}{35.5} = .816.$$

On dividing by the smallest quotient we have,

the relative number of atoms of K = $\frac{.833}{.816} = 1$.

" " " O = $\frac{2.45}{.816} = 3$.

" " " Cl = $\frac{.816}{.816} = 1$.

Hence the empirical formula is KClO_3 .

EXAMPLE 2. *An iron oxide has the composition Fe=70 percent and oxygen=30, percent. What is the formula of the compound?*

Dividing the percentage by atomic weight of the element we have :—

$$\text{Fe} = \frac{70}{56} = 1.25 \text{ and } \text{O} = \frac{30}{16} = 1.88.$$

On dividing by the lowest quotient, we have,

the relative number of atoms of Fe = $\frac{1.25}{1.25} = 1$,

" " " O = $\frac{1.88}{1.25} = 1.5$

Since atoms do not take part in fractions in chemical reactions, so to get the simplest whole number ratio multiply both by 2, then the ratio is 2:3.

Hence the formula is $\text{Fe}_2 \text{O}_3$.

EXAMPLE 3. *A compound has the composition Na=14.31% ; S=9.97% ; H=6.25% ; O=69.47%*

Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallisation.

In water, 2 gm. hydrogen is combined with oxygen
= 16 gms.

$\therefore 6.25$

"

$$= \frac{16}{2} \times 6.25 = 50$$

\therefore percentage of water $= 50 + 6.25 = 56.25$
 and percentage of oxygen $= 69.47 - 50 = 19.47$.

Dividing the percentages by atomic weights we have

$$\text{Na} = \frac{14.31}{23} = .62 ; \text{S} = \frac{9.97}{32} = .31 ; \text{O} = \frac{19.47}{16} = 1.21 ;$$

$$\text{H}_2\text{O} = \frac{56.25}{16} = 3.12$$

On dividing by the lowest quotient we have:—

$$\text{Relative number of atoms of Na} = \frac{.62}{.31} = 2$$

$$\text{S} = \frac{.31}{.31} = 1$$

$$\text{O} = \frac{1.21}{.31} = 4$$

$$\text{H}_2\text{O} = \frac{3.12}{.31} = 10$$

\therefore formula of the compound is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

EXAMPLE 4. Calculate the empirical formula of a compound with the following percentage composition:—

$\text{Cu} = 25.6\%$, $\text{S} = 12.8\%$, $\text{O} = 25.6\%$ and water $= 36.04\%$.

Dividing the percentage by atomic weight of each element, we have:—

$$\text{Cu} = \frac{25.6}{63.6} = .402, \text{S} = \frac{12.8}{32} = .4, \text{O} = \frac{25.6}{16} = 1.6 \text{ and}$$

$$\text{water} = \frac{36.04}{18} = 2$$

On dividing by the smallest quotient, we have,

$$\text{the relative number of atoms of Cu} = \frac{.402}{.4} = 1$$

the relative number of atoms of S = $\frac{.4}{.4} = 1$

“ “ “ O = $\frac{1.6}{.4} = 4$

“ “ molecules $H_2O = \frac{2}{.4} = 5$

Hence the empirical formula is $CuSO_4 \cdot 5H_2O$.

EXAMPLE 5. *The percentage composition of a clay is alumina $Al_2O_3 = 18.34\%$, silica, $SiO_2 = 64.64\%$ and potash $K_2O = 17.2\%$.*

Find the formula of the compound.

Dividing by molecular weight of each oxide its percentage, we have,

$$Al_2O_3 = \frac{18.34}{102} = .18, SiO_2 = \frac{64.64}{60} = 1.07,$$

$$K_2O = \frac{17.02}{94} = .18.$$

On dividing by the lowest quotient, we have,

the relative number of molecules of $Al_2O_3 = \frac{.18}{.18} = 1$

“ “ “ $K_2O = \frac{.18}{.18} = 1$

“ “ “ $SiO_2 = \frac{1.07}{.18} = 6$

Hence the formula is $K_2O, Al_2O_3, 6 SiO_2$.

Molecular Formula of a compound represents the actual number of atoms of each element present in a molecule of the compound. Since empirical formula represents the relative number of atoms and molecular formula the actual number of atoms in a molecule, it is

clear that molecular formula may either be the same as empirical formula or a (whole number) multiple of it.

Determination of Molecular Formulae. The molecular weight of a substance can be calculated if its vapour density is known, as it has already been proved in chapter VI that molecular weight is twice the vapour density. The nearest whole number obtained on dividing the molecular weight by empirical formula weight of the substance, gives the multiple N of empirical formula.

$$N = \frac{2 \text{ V. D.}}{\text{Empirical formula weight}}$$

The determination of molecular formula consists in :—

- (i) Finding the empirical formula from percentages.
- (ii) To find the formula weight of the empirical formula.
- (iii) To find molecular weight from vapour density by doubling it.
- (iv) To get the multiple of empirical formula on dividing molecular weight by empirical formula weight.

This is made clear by following examples :—

EXAMPLE 6. *A sample of mercury chloride contains 85.1% mercury and its vapour density is found to be 234.8. Find the molecular formula of the compound.*

Percentage of Mercury = 85.1

\therefore percentage of chlorine = $100 - 85.1 = 14.9$

Dividing by atomic weights of elements we have :—

$$\text{Hg} = \frac{85.1}{200} = .425 \text{ and } \text{Cl} = \frac{14.9}{35.5} = .419.$$

On dividing by lowest quotient we have,

the relative number of mercury atoms = $\frac{.425}{.419} = 1$

„ „ chlorine atoms = $\frac{.419}{.419} = 1$.

Hence empirical formula = HgCl .

Empirical formula weight = $200 + 35.5 = 235.5$.

Molecular weight of mercury chloride = $2 \times 234.8 = 469.6$

\therefore multiple of empirical formula = $\frac{469.6}{235.5} = 2$.

Hence molecular formula = $(\text{HgCl})_2 = \text{Hg}_2\text{Cl}_2$.

EXAMPLE 7. *Arsenic oxide contains 65.2% arsenic in it and its vapour density is found to be 229.5. Find the molecular formula of the compound. (As = 75).*

Percentage of As = 65.2 \therefore %age of oxygen = $100 - 65.2 = 34.8$.

Dividing percentages by atomic weights, we have :—

As = $\frac{65.2}{75} = .869$ and O = $\frac{34.8}{16} = 2.187$

On dividing by lowest quotient, we have,

the relative number of atoms of As = $\frac{.869}{.869} = 1$

„ „ „ O = $\frac{2.187}{.869} = 2.45$.

\therefore empirical formula = As_2O_5

Empirical formula weight = $150 + 80 = 230$.

Molecular weight = $2 \times 229.5 = 459$.

The multiple of empirical formula = $\frac{459}{230} = 2$.

Hence molecular formula = $(\text{As}_2\text{O}_5)_2 = \text{As}_4\text{O}_{10}$.

Problems

The percentage composition of compounds are :—

- [a] $H=2.22\%$ $P=34.8\%$ $O=62.9\%$
 [b] $H=1.6\%$ $N=22.23\%$ $O=76.17\%$
 [c] $Al=52.94\%$ $O=47.05\%$
 [d] $K=28.68$, $H=0.735$, $S=23.53$, $O=47.07$
 [e] $K=26.59$, $Cr=35.35$, $O=38.06$
 [f] $Na=29.11$, $S=40.50$, $=30.38$

Calculate their formulae.

2. Find the empirical formulae of the following substances whose % compositions are :—

- [a] $Mg=9.76$, $S=13.01$, $O=26.01$, $H_2O=51.22$
 [b] $Fe=20.14$, $S=11.51$, $O=23.02$, $H_2O=45.32$
 [c] $Ba=56.14$, $Cl=29.10$, $H_2O=14.75$
 [d] $Zn=22.65$, $S=11.15$, $O=22.30$, $H_2O=43.9$
 [e] $Cu=25.6$, $S=12.8$, $O=25.6$, $H_2O=36.04$
 [f] $Mg=11.96$, $Cl=34.87$, $H_2O=53.16$

3. A mineral on analysis gave the following percentage composition.

$$K=14.04, Al=9.72, Si=30.24, O=16$$

Calculate the formula of the mineral.

(P. U. 1923)

4. A clay on analysis gave the following percentage composition. What is the chemical formula of the clay.

$$Al_2O_3=39.77, H_2O=13.9, SiO_2=46.33.$$

5. In an arsenic oxide the amount of arsenic is 75.75% and its vapour density is 197.7. What is the molecular formula of the compound?

6. The percentage of tin in stannous chloride is

62.63 and its vapour density above 600°C is 188.8. Calculate the molecular formula of the compound.

7. What is the empirical formula of a substance having the following percentage composition :

Oxygen = 38.1%, Hydrogen = 0.8%, Phosphorus = 24.6% Sodium = 36.5% (Na = 23, P = 31, O = 16)

(P. U. 1938)

8. A substance on analysis was found to possess the following percentage composition : Na = 29.11% ; S = 40.5% ; O = 30.38%. Calculate the empirical Formula of the substance. (Na = 23, S = 32)

(P. U. 1946)

9. A substance on analysis was found to possess the following composition:

Na = 14.31%, S = 9.97%, O = 19.47%,

Water of crystallisation = 56.25%

Calculate the formula of the compound.

10. Calculate the empirical formulae of the compound with following percentage composition :—

[a] Mg = 9.79, N = 5.71, H = 1.63, P = 12.65, O = 26.12, H_2O = 44.08.

[b] Mn = 43.63, Cl = 56.36.

[c] Na = 36.8, H = .8, O = 38.2, P = 24.6.

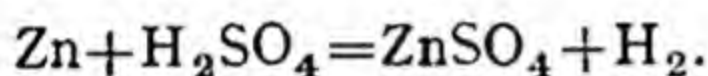
[d] K = 35.56, Fe = 17.02 ; C = 21.88 ; N = 25.53

Philip Ingboof Thumelent

CHAPTER X

CALCULATIONS BASED ON CHEMICAL EQUATIONS.

Chemical Equation is an expression which tells by means of formulae the nature and relative quantities of the substances reacting and formed in a chemical reaction e.g.



An equation, therefore, represents three things :—

[a] It represents the substances reacting and the substances formed or produced in the reaction.

[b] It represents the weights of reactants reacting and of the resultants produced.

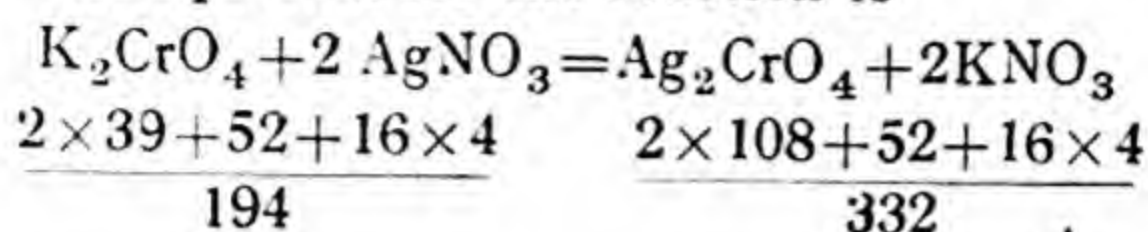
[c] An equation also represents the relative volumes of gases reacting or formed in a chemical reaction.

It is, therefore, possible to find out the weights or volumes of reactants that should react to produce definite weights or volumes of resultants. In this chapter calculations are therefore based on chemical reactions of substances. Following are the typical examples :—

TYPE I.

EXAMPLE 1. 100 m.l. of solution of potassium chromate are added to silver nitrate solution to precipitate 13.28 gms. of silver chromate. Find the amount of potassium chromate dissolved in 100 c.c. of the solution.

The equation for the reaction is



It is clear from the equation that—

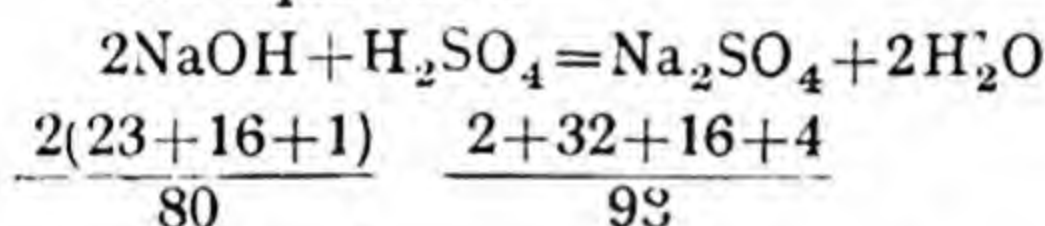
332 gms. silver chromate are produced from potassium chromate 194 gms.

\therefore 13.28 gms. silver chromate are produced from potassium chromate = $\frac{13.28 \times 194}{332} = 7.76$ gms.

Potassium chromate present in 100 m.l. = 7.76 gms.

EXAMPLE 2. *What weight of pure sulphuric acid is required to neutralize 100 gms. of caustic soda?*

The equation is—

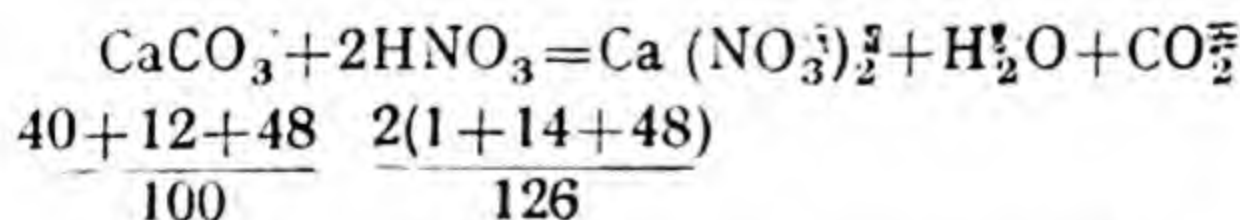


80 gms. caustic soda require 98 gms. sulphuric acid.

\therefore 100 gms. " " acid = $\frac{100 \times 98}{80} = 122.5$ gms.

EXAMPLE 3. *What weight of 10% nitric acid solution will be required to completely decompose 20 gms. of pure marble?*

The equation is—



100 gms. of marble are decomposed by nitric acid
126 gms.

∴ 20 gms. of marble are decomposed by nitric acid

$$\frac{126 \times 20}{100} = 25.2 \text{ gms.}$$

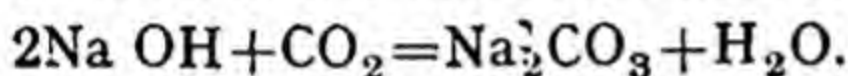
10 gms. acid nitric is present in 100 gms. solution

$$\begin{aligned} \therefore 25.2 \text{ gms. acid nitric are present in} &= \frac{25.2 \times 100}{10} \\ &= 252 \text{ gms. of solution.} \end{aligned}$$

Hence weight of nitric acid dil. reqd. = 252 gms.

EXAMPLE 4. *What weight of calcium carbonate must be decomposed by HCl to produce a quantity of carbon dioxide that will suffice for the conversion of 30 gms. of caustic soda into sodium carbonate?*
(Cal. U. 1903)

In such a case start first with the second part—

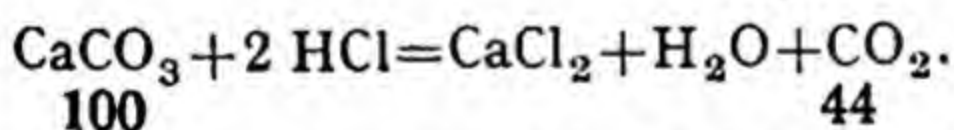


$$\begin{array}{cc} 80 & 44 \end{array}$$

80 gms. caustic soda require carbon dioxide = 44 gms.

∴ 30 gms. caustic soda require carbon dioxide

$$= \frac{30 \times 44}{80} = 16.5 \text{ gms. CO}_2.$$



44 gms. carbon dioxide is obtained from CaCO₃ 100 gms.

∴ 16.5 gms. carbon dioxide is obtained from CaCO₃

$$= \frac{100 \times 16.5}{44} = 37.5 \text{ gms. of calcium carbonate.}$$

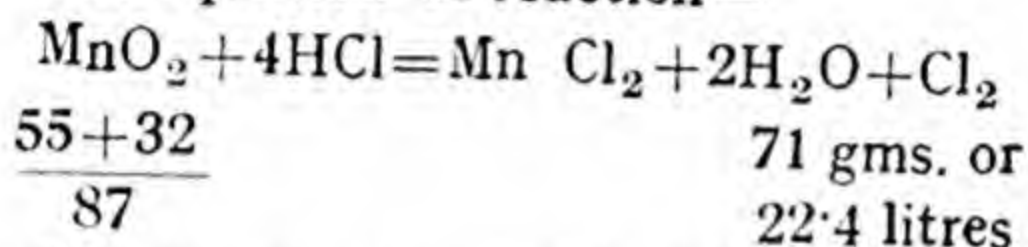
TYPE II

The volume-weight relationship of gases 22.4 litres are occupied at N. T. P. by one gram molecular weight

of any gas. This is also called **gram-molecular volume** or G. M. V. In these calculations it is also helpful to note that **1 m.l. of hydrogen weighs 0.00009 gms. at N. T. P.** Hence the weight of 1 m.l. of any gas at N. T. P. will be $\cdot 00009 \times$ density of the gas with respect to hydrogen.

EXAMPLE 5. *What is the volume of chlorine evolved by treating 29 gms. of manganese dioxide with excess of hydrochloric acid at 750 mm. pressure and 37°C.*

The equation of reaction—



87 gms. manganese dioxide evolve 22.4 litres Cl at N. T. P.

\therefore 29 gms. manganese dioxide evolve chlorine

$$= \frac{29 \times 22.4}{87} = 7.46 \text{ litres.}$$

$$P_o = 760$$

$$P = 750$$

$$V_o = 7.46$$

$$V = ?$$

$$T_o = 273$$

$$T = 273 + 37 = 310\text{A.}$$

$$\therefore V = \frac{P_o V_o}{T_o} \times \frac{T}{P} = \frac{760 \times 7.46 \times 310}{750 \times 273} = 8.59 \text{ litres}$$

Chlorine evolved at 37°C and 750 mm. = 8.59 litres.

TYPE III

Calculations regarding Purity of Substances. A chemical equation represents an ideal reaction between pure substances. In nearly all the reactions the substances used are not chemically pure. The impurity can be calculated thus—

EXAMPLE 6. *One gram of zinc containing only the oxide of zinc as an impurity, yielded on treatment with*

dilute sulphuric acid 130 m.l. of moist hydrogen at 16°C and 755 mm pressure. Calculate the percentage of zinc in the impure specimen of zinc. ($\text{Zn}=65.4$, Aq. tension at $16^{\circ}\text{C}=13.53$ mm.)

(P. U. 1914)

$$P_0 \approx 760$$

$$P = 755 - 13.53 = 741.47 \text{ mm.}$$

$V_0 = ?$

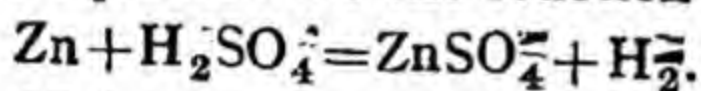
$$V = 130 \text{ m.l.}$$

$$T_o = 273$$

$$T = 273 + 16 = 289$$

$$\therefore V_o = \frac{PV}{T} \times \frac{T_o}{P_o} = \frac{130 \times 741.47 \times 273}{760 \times 289} = 120 \text{ m.l.}$$

The equation for the reaction is—



65.4

2 gms. or 22·4 litres.

22400 m.l. hydrogen is liberated by zinc = 65.4 gms.

$$\therefore 120 \text{ " " " " } = \frac{120 \times 65.4}{22400} \\ = .35 \text{ gms.}$$

Zinc oxide in the sample = $1 - .35 = .65$ gm.

1 gm. impure zinc sample contains zinc = .35 gm.

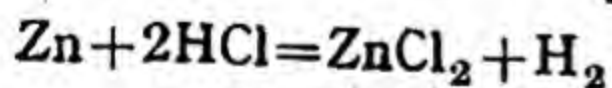
$$\therefore 100 \text{ gms.} \quad \text{“} \quad \text{“} \quad \text{“} \quad \text{“} \quad = .35 \times 100 = 35$$

$$\% \text{ Purity of zinc} = 35$$

EXAMPLE 7. A large lump of zinc is placed in 100 gms. of solution of hydrochloric acid. 150 m.l. of hydrogen at 15°C and 740 mm. pressure are evolved. Calculate the percentage of hydrochloric acid in the solution.

Vol. of hydrogen evolved = 150 m.l.s. at 15°C and 740 mm.

$$\text{Vol. at N.. T. P.} = \frac{150 \times 740 \times 273}{760 \times 288} = 138.4 \text{ m.l.}$$



73

22.4 litres

Now 22.4 litres of hydrogen are evolved from 73 gms. of HCl.

∴ 138.4 m.l. of hydrogen will be evolved from

$$\frac{73 \times 138.4}{22400} = .453 \text{ gms. of HCl.}$$

∴ 100 gms. of the acid solution contains .453 gms. of HCl.

∴ %age of the acid in solution = .453. **Ans.**

TYPE IV

Volume of gases reacting. These calculations are based upon Gay-Lussac's law of volumes which states "When gases react together they do so in volumes which bear a simple ratio to one another and to the gaseous products formed.

EXAMPLE 8. *What volume of oxygen at 0°C and 760 mm. pressure is required to effect the complete combustion of 12 litres of marsh gas at 15°C and 750 mm. pressure.*

(P. U. 1911)

The volume of 12 litres marsh gas at N. T. P. is calculated first :—

$$P = 750 \text{ mm.}$$

$$P_o = 760$$

$$T = 15 + 273 = 288 \text{ A.}$$

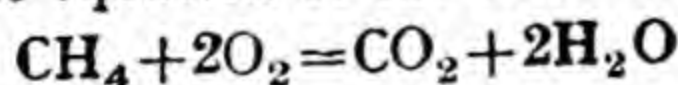
$$T_o = 273$$

$$V = 12 \text{ litres}$$

$$V_o = ?$$

$$\therefore V_o = \frac{PV}{T} \times \frac{T_o}{P_o} = \frac{750 \times 12 \times 273}{288 \times 760} = 11.23 \text{ litres.}$$

The equation of the combustion reaction is—



1 vol. 2 vols.

Thus from the equation it is clear that :—

1 volume of marsh gas requires for combustion

oxygen = 2 volumes.

$\therefore 11.23$ litres marsh gas requires for combustion
oxygen $= 11.23 \times 2 = 22.46$ litres oxygen.

EXAMPLE 9. Find the weight of pottassium chlorate required for producing just en ough oxygen gas for the complete combustion of 312.35 litres of marsh gas at 540 mm. and 20°C .
(P. U. 1919)

The volume of 312.35 litres marsh gas at N. T. P. is calculated to be—

$$P = 540 \text{ mm.}$$

$$P_o = 760$$

$$T = 273 + 20 = 293 \text{ A.}$$

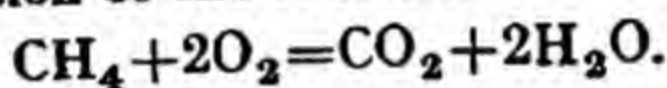
$$T_o = 273$$

$$V = 312.35 \text{ litres}$$

$$V_o = ?$$

$$\therefore V_o = \frac{PV}{T} \times \frac{T_o}{P_o} = \frac{312.35 \times 273 \times 540}{293 \times 760} = 206.78 \text{ litres}$$

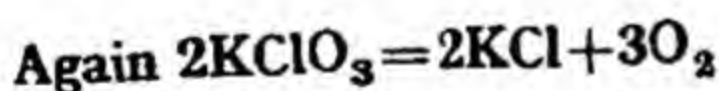
The equation of the reaction is—



1 vol. 2 vols.

1 volume marsh gas requires 2 vols. oxygen

$$\therefore 206.78 \text{ litres } \dots \dots \text{ oxygen} = 2 \times 206.78 \\ = 413.56 \text{ litres oxygen.}$$



$$245$$

$$67.2 \text{ litres}$$

$$(3 \times 22.4)$$

67.2 litres oxygen is obtained from $\text{KClO}_3 = 245$ gms.

$$\therefore 413.56 \dots \dots \dots = \frac{245 \times 413.56}{67.2} \\ = 1507.7 \text{ gms.}$$

Potassium chlorate required $= 1507.7$ gms.

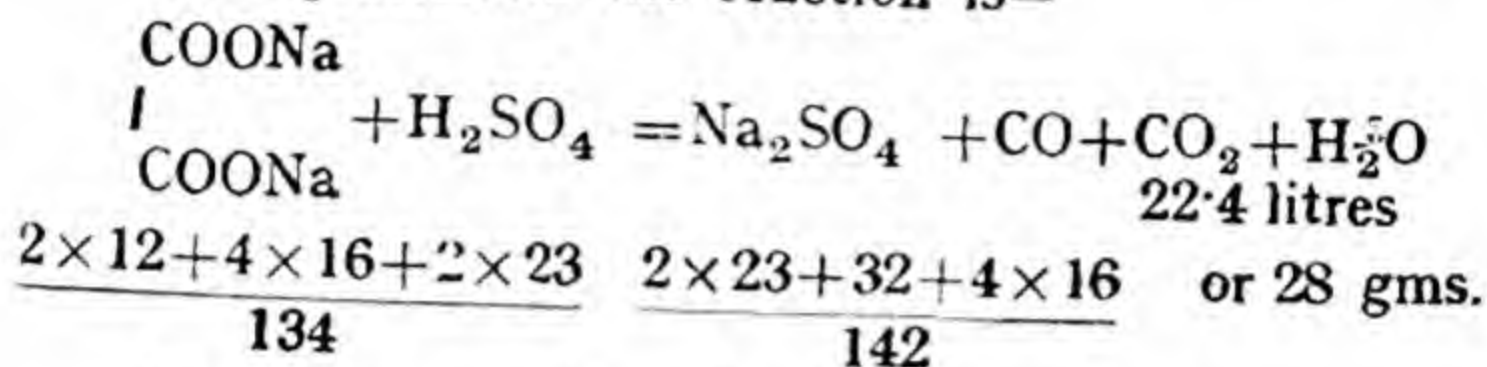
EXAMPLE 10. From one gram of sodium oxalate what weight of sodium sulphate can be obtained on ignition with sulphuric acid. And what volume of carbon

monoxide at 0°C and 760 mm. Pressure can be collected from the gases evolved.

$$(\text{Na}=23, \text{S}=32, \text{C}=12)$$

(P. U. 1926).

The equation for the reaction is—



(a) 134 gms. sod. oxalate forms sod. sulphate = 142 gms.

\therefore 1 gm. sod. oxalate forms sod. sulphate = $\frac{142}{134}$
= 1.059 gms. Ans.

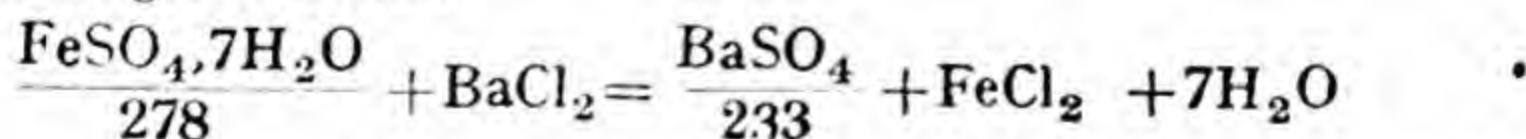
(b) 134 gms. sod. oxalate evolves $\text{CO} = 22.4$ litres
or 22400 m.l.

\therefore 1 gm sod. oxalate evolves $\text{CO} = \frac{22400}{134} = 167.1 \text{ m.l.}$

COMPLEX TYPE V.

In this case two or more reactions may be taking place side by side. The best way of calculation can be found out by careful examination of the problem.

EXAMPLE 11. 1.39 gm. of ferrous sulphate were dissolved in water and the solution was treated with excess of barium chloride solution, the precipitate of barium sulphate was formed. The precipitate was filtered, washed and dried and weighed 1.165 gms. Find the %age of sulphate radical in the green vitriol.



The sulphate radical of green vitriol has formed barium sulphate.

The weight of sulphate part = $\text{SO}_4 = 32 + 4 \times 16 = 96$.

233 gms. barium sulphate contains $\text{SO}_4 = 96$ gms.

$$\therefore 1.165 \quad \text{..} \quad \text{..} \quad \text{..} \quad = \frac{96 \times 1.165}{233} \\ = .48 \text{ gms.}$$

The amount of sulphate in barium sulphate is the same as in green vitriol.

$\therefore 1.39$ gms. ferrous sulphate contains .48 gm, SO_4 .

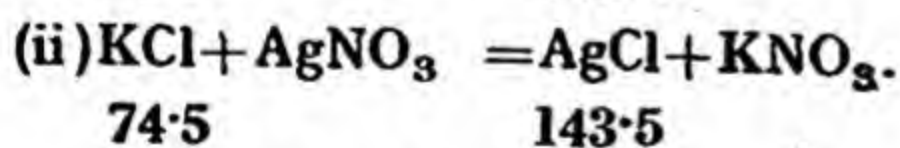
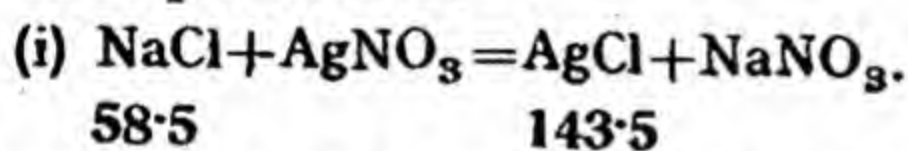
$$\text{Hence } 100 \quad \text{..} \quad \text{..} \quad \text{..} \quad \text{SO}_4 = \frac{.48 \times 100}{1.39} \\ = 34.5\% \text{ sulphate.}$$

EXAMPLE 12. 2.2 gms. of a mixture of sodium and potassium chlorides on treatment with silver nitrate formed 4.6 gms. of silver chloride. Find the percentage of each in the mixture. ($\text{Na} = 23, \text{K} = 39, \text{Ag} = 108, \text{Cl} = 35.5$).

Let x be the amount of sodium chloride in the mixture

Then potassium chloride in the mixture is $2.2 - x$ gm.

The equations are—



From equation (i)

58.5 gms. common salt gives 143.5 gms silver chloride

$$\therefore x \text{ gm.} \quad \text{..} \quad \text{..} \quad \text{gives AgCl} = \frac{143.5 x}{58.5} \text{ gms..... (a)}$$

From equation (ii)

74.5 gms. KCl gives $\text{AgCl} = 143.5$ gms.

$$\therefore (2.2-x) \text{ gm. KCl gives AgCl} = \frac{143.5(2.2-x)}{74.5} \text{ gms. (b)}$$

$$\therefore \text{Total weight of silver chloride} = \frac{143.5 x}{58.5} + \frac{143.5(2.2-x)}{74.5}$$

This is the weight of silver chloride actually obtained.

$$\therefore \frac{143.5 x}{58.5} + \frac{143.5(2.2-x)}{74.5} = 4.6$$

$$\text{or } x \left(\frac{143.5}{58.5} - \frac{143.5}{74.5} \right) = 4.6 - \frac{143.5 \times 2.2}{74.5}$$

$$\text{or } x(2.452 - 1.926) = 4.6 - 3.238 = .362.$$

$$\text{or } .526 x = .362.$$

$$\therefore x = \frac{.362}{.526} = .68.$$

2.2 gms. of the mixture contains .68 gm. sodium chloride.

$$\therefore 100 \text{ gms. " " " NaCl} = \frac{.68 \times 100}{2.2} = 30.9 \%$$

$$\text{Percentage of KCl} = 100 - 30.9 = 69.1.$$

$$\text{NaCl} = 30.9\% \text{ and KCl} = 69.1\%.$$

Problems.

1. What weight of potassium nitrite and volume of oxygen would be formed by heating 50.5 gms. of potassium nitrate.

2. Ten grams of pure marble are dissolved in hydrochloric acid. Calculate the volume of carbon dioxide which would be evolved if measured at 25°C. and 750 m.m. pressure.

[Atomic weights : $\text{Ca}=40$, $\text{C}=12$, $\text{O}=16$]

(P. U. 1939)

3. A large lump of Zinc is placed in 100 gms. of a solution of HCl . 150 m. l. of H_2 at 15°C . and 740 m.m. are evolved. Calculate the percentage of HCl in the solution.

(P.U. 1941)

4. Calculate the weight of slaked lime required to decompose completely 6 gms. of ammonium chloride and what weight of each product would be formed?

5. One gm. of the chloride of a metal when treated with excess of Ag NO_3 produced .965 gm. of dry AgCl . Calculate the atomic weight of the metal, given that it closely resembles Barium in its properties.

6. How many grams of Bromine are required to completely convert 8.8 gms. of Benzene into monobromobenzene. (assume the reaction be quantitative)

(P. U. 1932)

7. What weight of silver nitrate would be required for the complete decomposition of Ferric chloride.

8. If hydrochloric acid contains 20% by weight of hydrogen chloride, the remaining being water what weight of this acid will be required for reacting completely with 50 gms. of calcium carbonatic? Will any gas be evolved? If so what will be its weight?

(Atomic weights : $\text{Ca}=40$, $\text{C}=12$, $\text{O}=16$, $\text{Cl}=35.5$, $\text{H}=1$)

(P. U. 1937)

9. A fuel contains 90 percent carbon and 10 percent incombustible matter. What volume of air at N. T. P. (containing 21 percent by volume of oxygen) will be required to burn completely one kilogram of this fuel?

[Atomic weight of carbon=12]

10. Calculate the volume of sulphur dioxide which would be required to convert the whole of sulphur in 20 m.l. of sulphuretted hydrogen into free sulphur.

11. What volume of hydrogen gas measured, in dry condition, at 20°C and 750 mm. pressure will be evolved by dissolving completely 20 grams of zinc in excess of hydrochloric acid? [Atomic weight of zinc = 65].

(P. U. 1936)

12. 0.1931 gm. of a diamond gave, on complete combustion, 0.704 gm. of CO_2 . Calculate the percentage purity of the diamond.

(P. U. 1936)

13. A sample of dolomite contained 54% CaCO_3 , 42% MgCO_3 , and 4% of clay. Calculate the volume of CO_2 evolved at 10°C and 750 mm. pressure which would be evolved on treating 10 gms. of the sample with excess of dil. acid.

14. Air contains 21% oxygen by volume. Calculate the theoretical volume of air which will be required for burning completely 500 cubic feet of acetylene gas (C_2H_2). All volumes are measured under the same conditions of temperature and pressure. Ans. 5952.4 cubic feet.

(P. U. 1937)

15. 10 m.l. of liquid carbon bisulphide (sp. gr 2.63) are burnt in oxygen thus ($\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$). Find the volume of oxygen to burn this liquid and the volume of resulting gases measured at N. T. P.

16. 1.60 gms. of a sample of ammonium sulphate on treatment with excess of sodium nitrate solution liberated 760 m.l. of dry nitrogen at 0°C and 448 mm. pressure. Find the percentage purity of ammonium sulphate.

[H = 1, N = 14, O = 16, S = 32, Na = 23]

(P. U. 1944)

17. What weights of zinc and sulphuric acid would be required to produce enough hydrogen to reduce completely 8.5 gms. of copper oxide to copper ?

[H=1, Zn=65, Cu=63.5, S=32, O=16.]

(P. U. 1944)

18. What volume of oxygen at N. T. P. is required to effect complete combustion of 100 m.l. of ethylene ?

Ans. 300 m.l.

19. What volume of oxygen at 18°C and 754 mm. pressure is liberated by 1.763 gms. KClO_3 when completely decomposed. What difference would there be in the volume, if this were collected and measured over water.

[Ag. Tension=15.5 mm.]

(P. U. 1919)

20. How much manganese dioxide and how much hydrochloric (33% HCl) will be required to furnish chlorine necessary to convert 40 gms. of potassium hydroxide completely into chlorate and chloride.

(P. U. 1926)

21. 8 gms. of pure Manganese dioxide are heated with excess of HCl and gas evolved is passed into a solution of KI. Calculate the weight of iodine that is liberated.

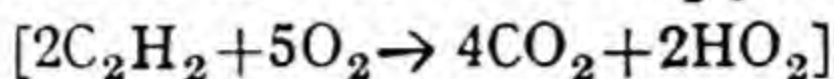
(Nagpur University 1933)

22. 100 m.l. of a gas were decompletely composed by heated tin, the tin being converted into stannous sulphide. The residual gas consisted of hydrogen and when passed over heated copper, gave 0.081 gram of water. V.D. of gas was 17. Deduce the formula of the gas.

(P. U. 1925)

23. What Vol. of oxygen would be required for the complete combustion of 200 m.l. of acetylene (C_2H_2)

and what would be the Volume of CO_2 produced.



(P. U. 1937)

24. 1.60 gms. of a sample of $(\text{NH}_4)_2\text{SO}_4$ on treatment with excess of NaNO_2 solution liberated 760 m.l. of dry hydrogen at 0°C and 448 mm. pressure. Find the percentage purity of $(\text{NH}_4)_2\text{SO}_4$.

25. How many gms. of common salt must be taken to make sufficient hydrochloric acid to produce when acting on an excess of zinc, 7.5 litres of hydrogen measured over water at 18°C and 600 mm. pressure.

[Ag. Tension = 15 mm.]

(Rangoon Inter)

26. A sample of dolomite contained 50% of CaCO_3 , 45% of MgCO_3 and 5% of clay. Calculate the volume of CO_2 measured at 10°C and 750 mm. pressure which would be evolved on treating 5 gms. of a sample with dil. HCl .

(Delhi Inter 1936)

27. In a certain experiment 10 litres of CO_2 at 27°C and 765 mm. pressure are required. How much marble of 96.5% purity would be required to prepare the above quantity of the gas at the experimental conditions.

(U. P. Board Inter 1944)

28. One litre of sulphur dioxide is mixed with one litre of hydrogen sulphide, both at N. T. P. Calculate the weight of each substance found after the reaction.

(U. P. Inter 1948)

29. A mixture of calcium and magnesium carbonate weighing 1.42 gms. was strongly heated until no further loss of weight was perceived. The residue

weighed 0.76 grams. What percentage of mixture was magnesium carbonate?

(U. P. Board Inter 1933)

30. One gm. of iron is converted into Ferric Chloride and the product is dissolved in water. What volume of H_2S at N. T. P. will be theoretically required to completely reduce the Ferric Chloride to Ferrous Chloride [$\text{Fe}=56$].

(Punjab Inter 1923)

31. 1.84 gms. of a mixture of CaCO_3 and MgCO_3 is strongly heated till no further loss of weight takes place. The residue weighs 0.96 gm. Find the percentage composition of the mixture.

(U. P. Board Inter 1943)

32. Ten gms. of native sulphur when burnt in air produce 6 litres of SO_2 at N. T. P. Find out the percentage of pure sulphur in the substance.

(Bombay Inter Science)

33. How much H_2SO_4 is required to decompose 100 gms. of chalk (CaCO_3) and how much calcium sulphate will be produced?

(Calcutta Inter 1910)

34. 3.60 gms. of a mixture of sodium and potassium chlorides gave with silver nitrate 7.74 gms. of silver chloride. What is the percentage of each salt in the mixture.

(U. P. Board Inter 1944)

35. What weight of aluminium metal when treated with excess of hydrochloric acid would give 39.3 m.l. of moist hydrogen measured at 13°C and 761 mm. pressure?

[Aq. Tension at $13^\circ\text{C}=11$ mm.]

Handwritten: H. J. Hughes / H. J. Hughes
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CHAPTER XI

VOLUMETRIC ANALYSIS.

Volumetric analysis is a method of determining the amount of a substance dissolved in a known volume of a given solution by measuring the volumes reacting.

A solution is said to be of **known strength** if the **amount of a substance present per m. l. or per litre in the solution is known**. In volumetric estimation, volume of suitable solution of known strength required to completely react with a known volume of the other solution is determined. The process is called **titration**.

APPARATUS.

The measurement of volume involves the use of graduated vessels. Some of the simple apparatus used are :—

Measuring cylinders, measuring flasks, **burettes** and **pipettes**.

Measuring cylinders are used to measure approximate volumes and are graduated in m. l. up to 100 m. l.

Measuring Flasks are graduated to contain a certain volume of liquid when filled upto a mark scratched on the neck. The flasks commonly in use are 100 m.l., 250 m. l. 500 m l. and 100 m. l.

Pipettes are graduated to deliver 5 m. l., 10 m. l. 20 m. l. or 25 m. l.

They are filled by sucking in the liquid a little above the mark, then it is pressed by the index finger.

The pressure is slowly released till the level of the liquid coincides with the mark, then it is delivered into a suitable vessel. The last drops should not be blown out but only touch it with the side of the vessel.

Always use a pipette with an unbroken point.

Burettes are graduated downward from 0 to 50 m. l., each m. l. being subdivided into one-tenths. They have either a glass stopper or a rubber tubing with pinch-cork and jet to regulate the flow of liquid. The air bubbles from this part must be driven out completely.

The readings should be taken at the start and at the end of the experiment to get the volume of the liquid used. In measurements **take the readings against the lower meniscus of the transparent liquids and the upper meniscus of deeply coloured liquids.**

The burette must be fixed vertical.

TERMS

The important terms used in volumetric analysis are explained below :—

Strength of a solution represents the amount dissolved per m. l. or per litre. **Standard solution** is that whose strength is known.

Titration is the process of finding the volume of a solution required exactly to react with a known volume of the other solution.

End point is point at which the reaction is complete.

Indicator is the reagent which indicates the end point by change in colour of the solution.

Equivalent weight of a substance is that weight which can react with or displace from a compound 1 gram hydrogen or 8 grams oxygen or any other chemical equivalent.

Normal strength of a solution is that in which an equivalent weight of the substance is dissolved in water and the solution is made to 1 litre. Such solutions are indicated as **N. HCl**, **N. KOH** or **N. H₂SO₄**.

A Normal solution is a standard solution but a standard solution may or may not be normal.

If a solution contains $\frac{1}{2}$ equivalent weight per litre, it is called a half-normal or **semi-normal** and is written $\frac{N}{2}$ or **.5 N**.

A solution which contains $\frac{1}{10}$ equivalent weight per litre, is known as a tenth normal or **deci-normal** and is expressed as $\frac{N}{10}$ or **.1 N**.

Similarly are expressed $\frac{N}{100}$, $\frac{N}{1000}$ or **10 N** solution.

Volumetric Analysis is subdivided under 3 heads :

1. **Acidimetry and Alkalimetry.**
2. **Oxidation and Reduction.**
3. **Precipitation.**

Acidimetry and Alkalimetry. In this part reactions of acid with bases are studied.

Neutralisation is the process by which a base completely reacts with or neutralises an acid to form a salt and water.

Equivalent weight of an acid is that weight of it which contains one part by weight of acidic or replaceable or ionic hydrogen.

The equivalent weight of HCl is 36.5, of HNO₃ is 63 and of H₂SO₄ is $\frac{2+32+64}{2}=49$

Equivalent weight of an acid $\frac{\text{Molecular weight}}{\text{Basicity}}$

Basicity of an acid is the number of replaceable hydrogen atoms present in a molecule of it.

Equivalent weight of a base is that weight of it which completely reacts with an equivalent weight of an acid.

The equivalent weight of NaOH is 40, of KOH is 56, of Ba (OH)₂ is $\frac{171}{2} = 85.5$ and of Na₂CO₃ is $\frac{106}{2} = 53$.

Equivalent weight of a base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Indicator.

The important indicators used in acidimetry and alkalimetry are Methyl orange, Litmus and Phenolphthalein.

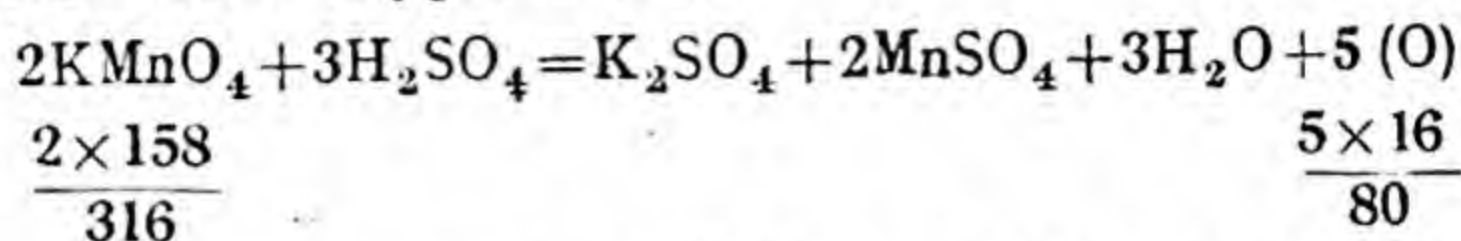
The indicator which should be used in a particular titration is shown in the chart below.

1. Strong acid and strong base. Use any indicator.
2. Strong acid and weak base (CO₃)'' Methyl orange
3. Organic acid and strong base Phenolphthalein.
4. Weak acid and weak base Litmus or phenolphthalein in presence of glycerine.

Oxidation and Reduction. The equivalent weight of an oxidising agent is that weight of it which contains 8 parts by weight of available or active oxygen.

Potassium permanganate KMnO₄ important oxidising agent used in the presence of dilute sulphuric acid.

The available oxygen in it is :—



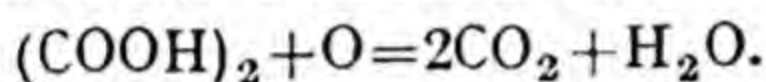
Since 80 parts oxygen is available from 316 parts KMnO_4

$\therefore 8$ " " " " " " 31.6 parts "

Eq. Wt. of $\text{KMnO}_4 = 31.6$.

The equivalent weight of a reducing agent is that weight of it which is oxidised by 8 parts by weight of oxygen.

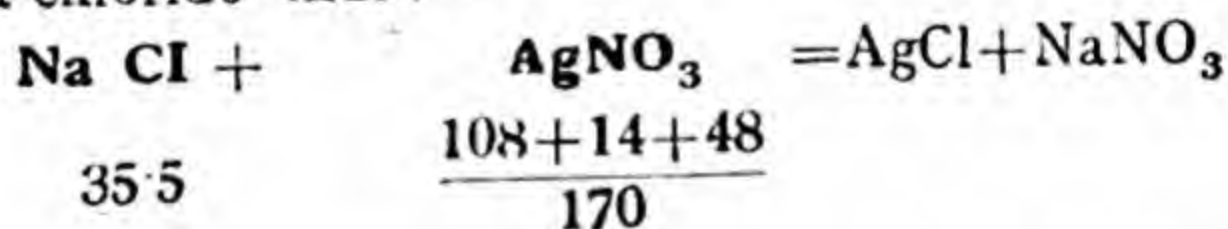
Oxalic acid is oxidised thus :—



16 parts oxygen can oxidise 90 parts of anhydrous and 126 parts of hydrated oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, hence its equivalent weight is 45 and 63 respectively.

No indicator is required because KMnO_4 itself is coloured.

Precipitation. Silver nitrate can react with a solution of a chloride thus :—



Since one gram equivalent (35.5) of ionic chlorine reacts with 170 parts of silver nitrate, hence its equivalent weight is 170.

Potassium chromate is used as the indicator.

CALCULATIONS.

The Normality of a solution is determined by dividing the weight of the pure substance in gms. per litre of the solution by its equivalent weight in grams.

$$\text{Normality} = \frac{\text{Wt. (in gms.) per litre}}{\text{equivalent Wt.}}$$

A given volume of a normal solution of any acid will neutralise the same volume of a normal solution of any alkali.

Thus 100 m.l. N HCl will neutralise 100 m.l. N. NaOH.

Similarly for other strengths. Hence the rule—

Equal volumes of solutions of same normality are equivalent to one another. Or

Equinormal solutions are all equi-volumetric.

$$\text{Volume used} \times \text{Normality} = \text{Volume used} \times \text{Normality}$$

a m.l. *b m.l.*

Thus if normality of one solution is $\frac{N}{10}$ and other to

be found is $\frac{N}{x}$ then $a \times \frac{N}{10} = b \times \frac{N}{x}$

$$\text{Hence the strength } \frac{N}{x} = \frac{a}{b} \times \frac{N}{10}$$

$$\text{or} = \frac{\text{Volume of the known soln.}}{\text{volume of the unknown soln.}} \times \text{strength of the known solution.}$$

$$= \frac{\text{known}}{\text{unknown}} \times \text{strength of known.}$$

Equivalent weight of important substances are given below:—

<i>Substance.</i>	<i>Formula.</i>	<i>Eq. Wt.</i>
Hydro chloric acid	HCl	26.5
Sulphuric acid	H ₂ SO ₄	49

<i>Substance</i>	<i>Formula</i>	<i>Eq. Wt.</i>
Nitric acid	HNO_3	63.
Oxalic acid	$(\text{COOH})_2$	45.
Oxalic hydrated	„ + $2\text{H}_2\text{O}$	63.
Acetic acid	CH_3COOH	60.
Caustic soda	NaOH	40.
Caustic potash	KOH	56.
Lime	$\text{Ca}(\text{OH})_2$	37.
Sodium carbonate	Na_2CO_3	53.
Sod. bicarbonate	NaHCO_3	84.
Ammonia	NH_3	17.
Potassium chloride	KCl	74.5.
Sodium „	NaCl	58.5.
Silver nitrate	AgNO_3	170.
Potassium permanganate	KMnO_4	31.6.
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	49.
Ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.
Ferrous ammonium sulphate (Mohr's salt)	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	392.
Chlorine	Cl	35.5.

(i) **Acidimetry and Alkalimetry.**

In these experiments the acid is always taken in the burette. A known volume of the alkali is taken in the titration flask and a few (2 or 3) drops of the suitable indicator (see indicators) is added, and the acid dropped in the alkali solution. The strength can be calculated as described above.

A. Calculation of strength of an alkali.

EXAMPLE 1. 20 m.ls. of caustic soda solution required 10 m. ls. of $\frac{N}{5}$ sulphuric acid. Calculate the strength of the caustic soda solution.

10 m. ls. of $\frac{N}{5} \text{H}_2\text{SO}_4$ ch. = 20 m. ls. of $\frac{N}{x} \text{NaOH}$.

Now $N_1 \times V_1 = N_2 \times V_2$.

$$\therefore \frac{N}{5} \times 10 = \frac{N}{x} \times 20$$

Hence $x = 10$.

So that strength of NaOH solution = $\frac{N}{10}$ i.e. $\frac{40}{10}$
= 4 gms. per litre.

EXAMPLE 2. 10. m.ls. of Na_2CO_3 solution require 8.5 m.ls. of $\frac{N}{10} \text{HCl}$. Calculate the strength of the Na_2CO_3 solution.

Suppose strength of the solution to be $\frac{N}{x}$

10 m.ls. of $\frac{N}{x} \text{Na}_2\text{CO}_3$ solution ch. = 8.5 m.ls. of $\frac{N}{10} \text{HCl}$

$$\therefore 10 \times \frac{N}{x} = 8.5 \times \frac{N}{10}$$

$$\text{or } x = \frac{10 \times 10}{8.5} = \frac{100}{8.5} = 11.77.$$

\therefore the strength of $\text{Na}_2\text{CO}_3 = \frac{N}{11.77}$ or $\frac{53}{11.77}$
= 4.5 gms./litre.

B. Calculation of strength of an acid.

EXAMPLE 3. 15 m.ls. of H_2SO_4 solution required 22.5 m.ls. of $\frac{N}{10} \text{NaOH}$. Calculate the strength of the acid solution.

$$15 \text{ m.l.s. of } \frac{N}{x} \text{H}_2\text{SO}_4 \text{ ch.} = 22.5 \text{ m.l. of } \frac{N}{10} \text{NaOH.}$$

$$\therefore 15 \times \frac{N}{x} = 22.5 \times \frac{N}{10}$$

$$\therefore x = \frac{15 \times 10}{22.5} = 6.66.$$

$$\therefore \text{the strength of the H}_2\text{SO}_4 \text{ solution} = \frac{N}{6.66}$$

$$\text{or } \frac{49}{6.66} = 7.36 \text{ gms./litre}$$

C. Estimation of Mixtures.

(i) Carbonate and bicarbonate of sodium :—

10 m.l.s. of a soln. carbonate and sod. bicarbonate was titrated against $\frac{N}{10}$ HCl, using phenolphthalein and methyl orange as indicators in two successive titrations and the volumes of the acid used were 4 m.l.s. and 10 m.l.s respectively. Calculate the strength of Na_2CO_3 and NaHCO_3 in the solution.

(When sodium carbonate is titrated against an acid with phenolphthalein as indicator, the carbonate cannot be completely neutralized but it is converted into the bicarbonate i.e. half the reaction takes place. Hence the volume of the acid required for full neutralization will be twice the volume in the 1st titration ($\therefore 2 \times 4 = 8$ m.l. in this case).

Now, in the presence of methyl orange, the volume of the bicarbonate present in the solution gets neutralised. Therefore the volume of the acid used for the 2nd titration is required for the neutralization of the sodium bicarbonate already present in the solution and that which has been formed during the 1st titration. This will require the same amount for its neutralization as is

used in the 1st titration. Therefore the amount of the acid that has been used for the neutralization of sodium bicarbonate is the difference between the 2nd and the 1st readings.

(i.e. $10 - 4 = 6$ m.ls. in this case). The question now resolves into the following :—

(i) 10 m. ls. of Na_2CO_3 solution ch = 8 m.ls. of $\frac{N}{10}\text{HCl}$

and (ii) 10 m. ls. of NaHCO_3 ch = 6 m.ls. of $\frac{N}{10}\text{HCl}$

(a) 10 m.ls. of $\frac{N}{x}\text{Na}_2\text{CO}_3$ ch. = 8 m.ls. of $\frac{N}{10}\text{HCl}$

$$\therefore 10 \times \frac{N}{x} = 8 \times \frac{N}{10}$$

$$\therefore x = \frac{10 \times 10}{8} = 12.5.$$

$$\therefore \text{Strength of } \text{Na}_2\text{CO}_3 = \frac{N}{12.5} \text{ or } \frac{53}{12.5} \\ = 4.24 \text{ gms./per litre}$$

(b) 10 m.ls. of $\frac{N}{x}\text{Na}_2\text{CO}_3$ ch = 6 m.ls. of $\frac{N}{10}\text{HCl}$,

$$\therefore 10 \times \frac{N}{x} = 6 \times \frac{N}{10}$$

$$\therefore x = \frac{10 \times 10}{6} = 16.66.$$

$$\text{Hence the strength of } \text{Na}_2\text{CO}_3 = \frac{N}{16.66} = \frac{84}{16.66} \\ = 5.04 \text{ gms./litre.}$$

(ii) **Caustic soda (or potash) and sodium carbonate :—**

20 m.ls. of a solution of caustic soda and sodium carbonate

were titrated against $\frac{N}{10}H_2SO_4$, and the following data were obtained:

Volume of the acid used (Phenolphthalein as indicator) = 15 m.l.

Volume of the acid used (Methyl orange as indicator) = 7 m.l.

Calculate the amounts of caustic soda and sodium carbonate per litre in the solution.

In this case the titration in the presence of phenolphthalein represents the neutralization of the whole of the caustic alkali and half of the carbonate, and the titration with methyl orange represents the neutralization of the remaining half of the carbonate. Therefore the first reading gives the volume of the acid required for complete neutralization of caustic soda and half neutralization of sodium carbonate and the 2nd reading gives the volume required for the neutralization of half of sodium carbonate.

Hence the volume required for the neutralization of caustic soda is the difference between the first and 2nd readings, and the volume required for the complete neutralization of sodium carbonate is double the 2nd reading.

(a) 20 m.l. of NaOH solution require 8 m.l.s.

(15 m.l.s. — 7 m.l.s.) of $\frac{N}{10}H_2SO_4$

and (b) 20 m.l.s. of Na_2CO_3 solution require 14 m.l.s.

(2 × 7 m.l.s.) of $\frac{N}{10}H_2SO_4$.

(a) 20 m.l.s. of $\frac{N}{x}NaOH$ ch = 8 m.l.s. of $\frac{N}{10}H_2SO_4$

$$\therefore 20 \times \frac{N}{x} = 8 \times \frac{N}{10}$$

$$x = \frac{20 \times 10}{8} = 25.$$

$$\text{Strength of NaOH} = \frac{N}{25} \text{ or } \frac{40}{25} = 1.6 \text{ gms./litre}$$

$$(b) 20 \text{ m.ls. of } \frac{N}{x} \text{Na}_2\text{CO}_3 = 14 \text{ m.ls. of } \frac{N}{10} \text{H}_2\text{SO}_4$$

$$\therefore 20 \times \frac{N}{x} = 14 \times \frac{N}{10}$$

$$\therefore x = \frac{20 \times 10}{14} = 14.3$$

$$\text{Hence strength of Na}_2\text{CO}_3 = \frac{N}{14.3} \text{ or } \frac{53}{14.3} = 3.7 \text{ gms./litre.}$$

(iii) Caustic Soda and Caustic Potash :—

6 gms. of a mixture of caustic soda and caustic potash are dissolved in 1 litre of the solution. 20 m.ls. of this solution required 24.28 m.ls. of $\frac{N}{10}$ HCl for complete neutralization. Calculate the percentage composition of the mixture.

The strength of the solution of NaOH and KOH = 6 gms./litre.

Volume of the mixture for each titration = 20 m.ls.

Suppose the Wt. of NaOH per litre = x gms.

Then the Wt. of KOH per litre = $(6-x)$ gms.

Therefore the strength of NaOH (in terms of normalities) = $\frac{x}{40} N$.

and that of KOH = $\frac{6-x}{56} N$.

Hence, we are to find out how much $\frac{N}{10}$ HCl will be required for 20 m.ls. of each of the above solutions.

Now 20 m.l.s. of $\frac{x}{40}$ N solution NaOH ch. = V. m.l. of $\frac{N}{10}$ HCl.

$$\therefore 20 \times \frac{x \times N}{40} = V \times \frac{N}{10}$$

$$V = \frac{20 \times 10 \times x}{40} = 5x \text{ m.l.}$$

and 20 m.l. $\frac{(6-x)}{56}$ N KOH = V_1 m.l. of $\frac{N}{10}$ HCl.

$$\therefore \frac{20 \times (6-x)}{56} N = \frac{V_1 \times N}{10}$$

$$\therefore V_1 = \frac{20 \times 10 \times (6-x)}{56} = \frac{25(6-x)}{7} \text{ m.l.}$$

Now the total volume of $\frac{N}{10}$ HCl used for 20 m.l.s of the solution = 24.28. m.ls.

$$\therefore V + V_1 = 5x + \frac{25(6-x)}{7}$$

$$\therefore 5x + \frac{25(6-x)}{7} = 24.28$$

$$\text{or } 35x + 150 - 25x = 169.96$$

$$\text{or } 10x = 169.96 - 150 = 19.96$$

$$\text{or } x = 2 \text{ very nearly.}$$

\therefore the strength of NaOH = 2 gms. per litre.

and that of KOH = $6 - 2 = 4$ gms. per litre.

Hence the percentage of NaOH = 33.33%.

and the percentage of KOH = 66.67%.

(iv) Hydrochloric and Sulphuric acids.

The given solution contains 10 gms. of hydrochloric and sulphuric acids. Calculate the strength of each of the acids from the following data.

10 m.ls. of the mixture requires 22.52 m.ls. of $\frac{N}{10}$

NaOH.

Wt. of the mixture of the acids per litre = 10 gms.

Suppose the Wt. of HCl " = x gms.

Then the Wt. of H_2SO_4 " = (10 - x) gms.

Hence the strength of HCl (in normality) = $\frac{x}{36.5} N$.

and the strength of H_2SO_4 " = $\frac{(10-x)}{49} N$

Now we are to calculate the volume of $\frac{N}{10}$ NaOH required for 10 m.ls. of each of the two solutions.

\therefore 10 m.ls. of $\frac{x}{36.5} N$ HCl ch. = V m.ls. $\frac{N}{10}$ HCl.

$$\frac{10 \times xN}{36.5} = \frac{V \times N}{10}$$

$$\therefore V = \frac{10 \times 10 \times x}{36.5} = \frac{100x}{36.5}$$

and 10 m.ls. of $\frac{10-x}{49} N$ H_2SO_4 ch. = V_1 m.ls. of $\frac{N}{10}$ HCl.

$$\frac{10 \times (10-x)N}{49} = V_1 \times \frac{N}{10}$$

$$\therefore V_1 = \frac{100 \times (10-x)}{49}$$

The total volume of HCl used = 22.52 m.ls.

$$\therefore \frac{100x}{36.5} + \frac{100(10-x)}{49} = 22.52.$$

$$\text{Or } 4900x + 36500 - 3650x = 22.52 \times 49 \times 36.5.$$

$$= 40277.$$

$$\text{Or } 1250x = 3777$$

$$x = \frac{3777}{1250} = 3.02 \text{ gms.}$$

\therefore Strength of $\text{HCl} = 3.02 \text{ gms. per litre}$

$$\text{Or } \frac{3.02}{36.5} = .0828 \text{ N.}$$

and strength of $\text{H}_2\text{SO}_4 = 6.98 \text{ gms. per litre}$

$$\text{Or } \frac{6.98}{49} = .143 \text{ N.}$$

(d) Determination of equivalents of acids and alkalis. In this case, a known weight of the acid is dissolved in water to a known volume, and the solution is titrated against a standard alkali. The equivalent weight is determined as follows.

Supposing 5 gms. of the acid are dissolved in 1 litre of the solution.

and 10 m.l.s. of this acid solution require 10.2 m.l.s.

of $\frac{N}{10} \text{NaOH.}$

Now 10 m.l.s. of the acid ch. = 10.2 m.l.s, of $\frac{N}{10} \text{NaOH.}$

$$\text{Then normality of the acid} = \frac{N}{10} \times \frac{10.2}{10}$$

$$= .102 \text{ N.}$$

Now suppose the equivalent Wt. of the acid = x

Then the strength of the acid is given to be 5 gms.
per litre.

$$\therefore .102x = 5.$$

$$\text{Or } x = \frac{5}{.102} = 49.02$$

Hence the equivalent weight of the acid = **49.02**.

N.B.—If the basicity of the acid be given, its molecular weight can be determined by multiplying the equivalent weight by basicity.

$$\text{Eq. Wt.} \times \text{basicity} = \text{molecular Wt.}$$

(V) .32 gm. of a dibasic organic acid required 71.1 m.ls. of $\frac{N}{10}$ NaOH for neutralization. Calculate the molecular weight of the acid.

71.1 m.ls. of $\frac{N}{10}$ NaOH will be equivalent to 71.1

m.ls. of $\frac{N}{10}$ acid

\therefore .32 gms. of the acid produce 71.1 m.ls. of $\frac{N}{10}$ acid

Hence 1 litre of $\frac{N}{10}$ acid will contain

$$\frac{.32 \times 1000}{71.1} \text{ gms.}$$

and 1 litre N. acid will contain $\frac{.32 \times 1000 \times 10}{71.1} \text{ gms.}$

of the acid = 45.

\therefore equivalent Wt. of the acid = 45

Basicity = 2,

\therefore molecular weight = $45 \times 2 = 90$

(e) **Determination of the number of molecules of water in the Crystals of an acid (oxalic acid, citric acid etc.) :—**

A known weight of crystals of the acid is dissolved in a known volume of solution and the solution titrated against standard alkali. From the formula of the an-

hydrous acid, the equivalent weight of the anhydrous acid is calculated and its strength per litre calculated. The difference in the calculated (anhydrous) and the given strength (hydrated), gives the amount of water of crystallisation present in that weight of the anhydrous acid. From this the weight of water present with one gram molecule is calculated, which when divided by 18, gives the number of molecules of water present in the molecule of the acid.

6 gms. of oxalic acid crystals were dissolved in 1 litre of the solution. On titration, 10 m.l.s. of the $\frac{N}{10}$ NaOH solution required 10.5 m.l.s. of the acid. Calculate the number of molecules of water of crystallisation in the crystals of the acid.

$$10 \text{ m.l.s. of } \frac{N}{10} \text{ NaOH ch.} = 10.5 \text{ m.l.s. of the acid.}$$

$$\therefore \text{ the normality of the acid} = \frac{N}{10} \times \frac{10}{10.5} = \frac{N}{10.5}$$

The formula of crystalline oxalic acid may be represented as $\left. \begin{array}{l} \text{COOH} \\ | \\ \text{COOH} \cdot x \text{ H}_2\text{O. where} \\ x \text{ stands for number of} \\ \text{molecules of water of} \\ \text{crystallisation.} \end{array} \right\}$

\therefore the equivalent weight of anhydrous acid is 45.

$$\begin{aligned} \text{Hence the strength of the anhydrous acid} &= \frac{45}{10.5} \\ &= 4.286 \text{ gms. per litre.} \end{aligned}$$

Now the strength of the hydrated acid (crystals)
= 6 gms. per litre.

$$\therefore 4.286 \text{ gms. of the anhydrous acid combines with } 6 - 4.286.$$

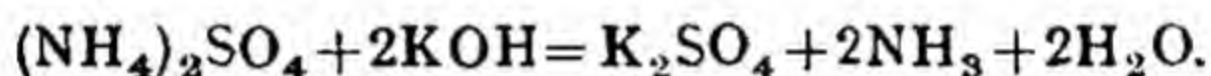
= 1.714 gms. of water.

∴ 90 gms. will combine with $\frac{1.714 \times 90}{4.286} = 35.9$ gms.
of water.

∴ the number of molecules of water = $\frac{35.9}{18}$
= 1.99 = 2.

(f) **Kjeldahl's Method** for the estimation of nitrogen in organic substances.

When a nitrogenous organic substance is heated with concentrated sulphuric acid, the nitrogen is converted into ammonium sulphate. The solution so obtained is then heated in a flask, with caustic potash when ammonia gas is evolved.



The ammonia so obtained can be estimated by passing into a known volume of a standard solution of an acid. The acid is neutralized by the ammonia, and the strength of the residual acid is determined by titration against standard alkali. From the amount of the acid used the amount of ammonia is calculated and from this the amount of nitrogen present in the known weight of the substance is obtained.

(i) 1.56 gms. of a substance, on being kjeldahlised gave ammonia that was passed into 50 m.ls. of N. H_2SO_4 . The acid left unneutralized was found to require 24 m.ls. of N. KOH. Calculate the percentage of nitrogen in the compound.

The unneutralized acid required 24 m.ls. of N. KOH. which is equivalent to 24 m.ls. of N acid.

Hence the amount of acid that was left unneutralized was 24 m.ls. of N acid.

The amount of the acid taken = 50 m.ls. of N acid

∴ The amount of acid neutralized by $\text{NH}_3 = 50 - 24$
 $= 26$ m.ls. of N acid.

Now 26 m.ls. of normal acid will require 26 m.ls. of N. ammonia.

∴ the amount of ammonia formed = 26 m.ls. of N. NH_3 .

(Equivalent of ammonia being 17) $= \frac{26 \times 17}{1000}$ gms.

Now 17 gms. of ammonia contain 14 gms. of nitrogen

Hence $\frac{26 \times 17}{1000}$ gms. of ammonia will contain

$\frac{26 \times 17 \times 14}{1000 \times 17}$ gms. of nitrogen

Now $\frac{26 \times 14}{1000}$ gms. of nitrogen is present in 1.56 gms. of the substance.

Hence the percentage of nitrogen $\frac{26 \times 14 \times 100}{1000 \times 1.56}$
 $= 23.30$.

(ii) By Kjeldahl's method, 0.59 gm. of an organic substance required 15 m.ls. of N. H_2SO_4 for the neutralization of ammonia. Calculate the percentage of nitrogen in the substance.

0.59 gm. of the substance gave ammonia that neutralized 15 m.ls. of N H_2SO_4 .

But 15 m.ls. of N H_2SO_4 ch. = 15 m.ls. of N. NH_3 .

∴ 15 m.ls. of N. NH_3 are obtained from 0.59 gm. of the substance.

Now 15 m.ls. of N. NH_3 will contain $\frac{17 \times 15}{1000}$ gms. of NH_3 .

and because 17 gms. of ammonia contain 14 gms. of nitrogen, the amount of nitrogen present in the ammonia formed

$$= \frac{17 \times 15}{1000} \times \frac{14}{17} = 0.21 \text{ gm.}$$

\therefore 0.59 gm. of the substance contains 0.21 gm. of nitrogen.

Hence the percentage of nitrogen = $\frac{0.21 \times 100}{0.59} = 35.6$

(g) Preparation of a solution of a known strength from a standard solution.

Exercise :— Prepare a decinormal solution of hydrochloric acid from the hydrochloric acid on the bench.

Take 10 m.l.s. of the hydrochloric acid from the bench, and dilute it to 100 m.l.s. in a graduated flask. Now titrate this solution against standard alkali and calculate the normality by the method described above.

Suppose the solution is $\frac{N}{7}$. Now we have to prepare

$\frac{N}{10}$ solution from the $\frac{N}{7}$ solution. Suppose V m.l.s. of

$\frac{N}{7}$ soln. is equivalent to 100 m.l.s. of $\frac{N}{10}$ solution.

$$\text{Then } V \times \frac{N}{7} = 100 \times \frac{N}{10}$$

$$\text{Or } V = 100 \times \frac{N}{10} \times \frac{7}{N} = 70 \text{ m.l.s.}$$

\therefore take 70 m.l.s. of the $\frac{N}{7}$ solution and dilute it to

100 m.l.s. This will give $\frac{N}{10}$ solution

(ii) You are given caustic soda solution whose strength is 5 gms. per litre. From this solution prepare

$$\frac{N}{20} \text{NaOH solution.}$$

Strength of the solution = 5 gms./litre.

$$\therefore \text{strength in normality} = \frac{5}{40} N = \frac{N}{8}.$$

Suppose V m.ls. of $\frac{N}{8}$ NaOH solution is equal to 100

$$\text{m.ls. } \frac{N}{20} \text{ solution}$$

$$\text{Then } V \times \frac{N}{8} = 100 \times \frac{N}{20}$$

$$\text{Or } V = 100 \times \frac{N}{20} \times \frac{8}{N} = 40 \text{ m.ls.}$$

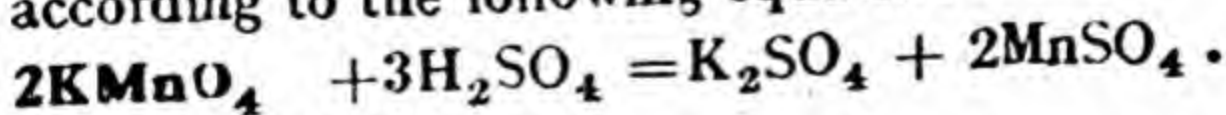
\therefore take 40 m.ls. of $\frac{N}{8}$ solution and dilute it to 100

m.ls. This will give $\frac{N}{20}$ solution

(ii) Oxidation and Reduction.

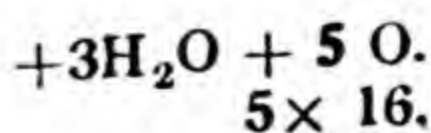
This type of volumetric exercises consists in titrating a reducing agent (Ferrous Salts, or Oxalic acid) against an oxidising agent (Potassium Permanganate). Potassium permanganate is always taken in the burette.

a. Equivalent Weights :—Potassium Permanganate acts as an oxidising agent in the presence of sulphuric acid according to the following equation—



$$2(39 + 55 + 64)$$

$$= 2 \times 158 = 316$$



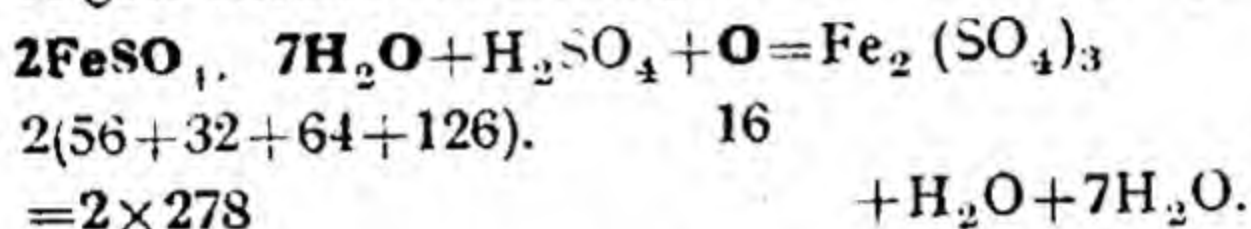
$$5 \times 16,$$

This oxygen oxidises the solution into which the permanganate solution is thus added. From the equation we find that 316 parts by weight of potassium permanganate give 80 parts of oxygen, according to the definition, therefore the equivalent weight of potassium permanganate is 316, so that the normal solution of potassium permanganate contains 31.6 gms. of the substance in one litre.

The substances that are titrated against potassium permanganate are—

1. Ferrous Sulphate, $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$

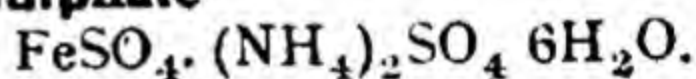
It gets oxidized according to the following equation.



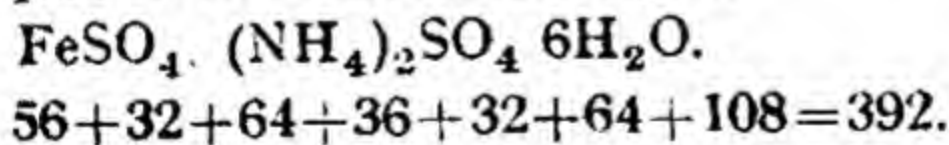
So that 8 gms. of oxygen will combine with 278 gms. of the salt.

Hence the equivalent of the hydrated salt is 278, whereas that of the anhydrous salt will be 152.

2. Ferrous Ammonium Sulphate

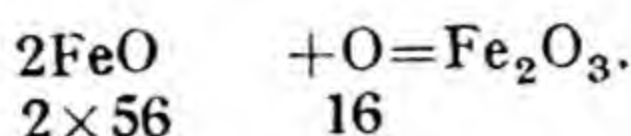


The equation for the reaction with oxygen being similar to the one stated in (1), its equivalent weight also is equal to its molecular weight.

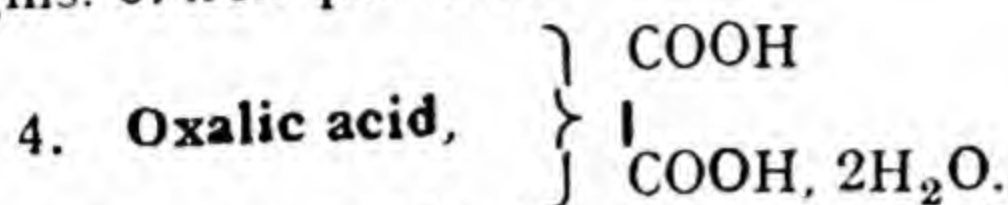


Hence the equivalent weight of the crystalline salt is 392 and that of the anhydrous salt is 284.

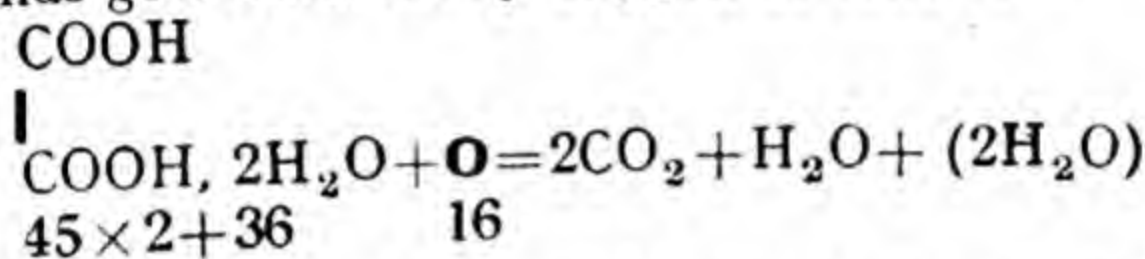
3. Equivalent Weight of Iron :—As shown above, the equivalent weight of iron will also be equal to its atomic weight when it is converted from the ferrous to the ferric state.



So that for 16 gms. of oxygen 112 gms. of iron are required and for 8 gms., 56 gms. will be required. A normal solution of a ferrous salt, therefore, contains 56 gms. of iron per litre.



It has gets oxidised by oxygen as follows—



Hence its equivalent weight is 45 when anhydrous and 63 when crystalline.

In titrations with oxalic acid, the solution has to be kept at a temperature of about 60°C , otherwise the reaction does not take place.

N.B.—In all titrations with potassium permanganate a few m.ls. of sulphuric acid must be added to the solution, after it has been measured out by means of a pipette. During and after titrations, the solution must remain clear and show an end point of slight pink colour. If it gives a brown precipitate or colouration, it means that enough sulphuric acid has not been added to the solution. In the absence of sulphuric acid hydrated oxide of manganese gets precipitated.

1. Calculations of Strengths of Solutions.

b. Exercises :—1. To prepare an $\frac{N}{10}$ solution of

potassium permanganate and to find out the strength of the given ferrous sulphate, ferrous ammonium sulphate or oxalic

acid solutions, 10 m.ls. of each of the solution requiring 12.5 m.ls. of the KMnO_4 solution.

The normal solution of KMnO_4 contains 31.6 gms. of the substance in one litre. Therefore in order to prepare $\frac{N}{10}$ solution, the strength will be 3.16 gms. per litre. So weigh out 3.16 gm. of the substance in watch glass and add it into a 100 m.ls. flask, shaking it continuously and make the volume upto 100 m.ls.

Take this solution in the burette and titrate against the given solution. **A pink colour gives the end point. In the case of oxalic acid, the solution has to be kept at 60°C**

Calculation—

(i) 10 m.ls. of the $\frac{N}{x}$ solution ch. = 12.5 m.ls. of $\frac{N}{10}$ KMnO_4 .

$$\therefore 10 \times \frac{N}{x} = 12.5 \times \frac{N}{10}$$

$$\therefore x = \frac{10 \times 10}{12.5} = \frac{100}{12.5} = 8.$$

$$\text{The strength of the solution} = \frac{N}{8}.$$

Now (i) in the case of ferrous sulphate the equivalent weight of the hydrated salt is 278, that of anhydrous salt 152 gms.

a. Strength of the hydrated salt is $\frac{278}{8} = 34.75$ gms. per litre.

b. The strength of anhydrous FeSO_4 will be $\frac{152}{8} = 19$ gms. per litre.

c. The amount of iron per litre (equivalent of iron = 56) will be $\frac{56}{8} = 7$ gms. per litre

(ii) The equivalent of ferrous ammonium sulphate is 392.

\therefore Its strength = $\frac{392}{8} = 49$ gms. per litre

(iii) The equivalent of oxalic acid crystals is 63 and that of the anhydrous acid is 45,

The respective strengths, therefore, are :—

a. Crystals— $\frac{63}{8} = 7.875$ gms. per litre.

b. Anhydrous— $\frac{45}{8} = 5.625$ gms. per litre.

2. Determination of the number of molecules of water of crystallisation [See this Chapter (e) above].

(i) 5 gms. of oxalic acid crystals are dissolved in one litre of solution. 10 m.l.s. of this solution required 7.95 m.l.s. of $\frac{N}{10}$ KMnO_4 . Calculate the number of molecules of water of crystallisation in oxalic acid.

10 m. ls. of the $\frac{N}{x}$ oxalic acid = 7.95 m.l.s. of $\frac{N}{10}$ KMnO_4 .

$$\therefore 10 \times \frac{N}{x} = 7.95 \times \frac{N}{10}$$

$$\therefore x = \frac{100}{7.9} = 12.66$$

$$\therefore \text{Strength of oxalic acid} = \frac{N}{12.66}$$

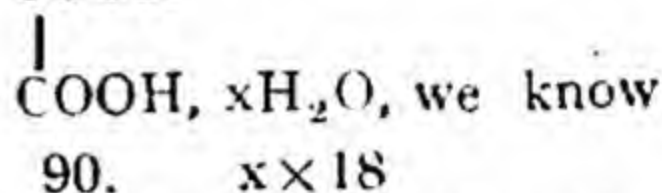
Now the equivalent weight of anhydrous oxalic acid = 45.

$$\therefore \text{strength of anhydrous oxalic acid} = \frac{45}{12.66} = 3.55 \text{ gms./litre.}$$

Strength of oxalic acid crystals = 5 gms. per litre.

$$\therefore \left. \begin{array}{l} \text{amount of water attached} \\ \text{to 3.55 gms. of oxalic acid} \\ \text{anhydrous} \end{array} \right\} = 5 - 3.55 = 1.45 \text{ gms.}$$

But from the formula COOH



that the molecular weight of anhydrous oxalic acid = 90.

$$\therefore \text{weight of water with 90 gms.} = \frac{1.45 \times 90}{3.55} = 36.8.$$

$\therefore 18x = 36.8$ where x is the number of molecules.

$$\therefore \text{the number of molecule of water of crystallisation} = \frac{36.8}{18} = 2.$$

(ii) Calculate the number of molecules of water of crystallisation in ferrous ammonium sulphate from the following data.

Strength of the solution = 14 gms. per litre.

10 m.ls. of the solution require 5.35 m.ls. of $\frac{N}{15} \text{KMnO}_4$.

10 m.ls. of $\frac{N}{x}$ ferrous salt solution ch. = 5.35 m.ls.

of $\frac{N}{15} \text{KMnO}_4$

$$\therefore 10 \times \frac{N}{x} = 5.35 \times \frac{N}{15}.$$

$$x = \frac{15 \times 10}{5.35} = 28.$$

$$\therefore \text{strength of the solution} = \frac{N}{28}.$$

The equivalent of anhydrous ferrous ammonium sulphate $(\text{FeSO}_4) \cdot (\text{NH}_4)_2\text{SO}_4 \cdot (x\text{H}_2\text{O}) = 284$. (See above).

284

18 x.

(where x is the number of molecules of water)

$$\therefore \text{strength of the anhydrous salt} = \frac{284}{28} = 10.15 \text{ gms.}$$

per litre.

But strength of the crystals = 14 gms. per litre.

$$\therefore \text{amount of water with } 10.15 \text{ gms. of anhydrous salt} \\ = 14 - 10.15 = 3.85 \text{ gms.}$$

The molecular weight (from the formula given above) of the anhydrous salt = 284.

$\therefore 10.15$ gms. combine with 3.85 gms. of water.

$$\therefore 284 \text{ gms. combine with } \frac{3.85 \times 284}{10.35} = 103 \text{ gms.}$$

$$\therefore 18x = 103.$$

$$x = \frac{103}{18} = 5.8 = 6.$$

\therefore number of molecules of water of crystallisation in ferrous ammonia sulphate = 6.

3. **Strength of a Ferric Salt**;—To calculate the amount of iron per litre in the given ferric salt solution.

Take 50 m.ls. of the given solution in **Bunsen Valve Flask**, and reduce the ferric salt into the ferrous state by means of magnesium powder and sulphuric acid. The total absence of the ferric salt is tested by means of potassium sulphocyanide solution which gives no red colouration with a ferrous salt. When the reduction is complete, make the solution upto 100 m.ls. and titrate

10 m.ls. of this solution against standard KMnO_4 solution and calculate the strength from the following data:—

Volume of the ferric salt solution taken = 50 m.ls.

Volume to which the solution is made after reduction (II) } = 100 m.ls.

Volume of the solution (II) taken for each titration } = 10 m.ls.

Volume of $\frac{N}{10}$ KMnO_4 solution used for titration } = 8 m.ls.

$\therefore 8$ m.ls. of $\frac{N}{10}$ KMnO_4 ch. = 10 m.ls. of $\frac{N}{x}$ ferrous salt.

$$\therefore 8 \times \frac{N}{10} = 10 \times \frac{N}{x}.$$

$$\therefore x = \frac{100}{8} = 12.5.$$

$$\therefore \text{strength of the ferrous salt solution} = \frac{N}{12.5}$$

The equivalent of iron = 56.

$$\therefore \text{amount of iron per litre} = \frac{56}{12.5} = 4.48 \text{ gms.}$$

Now the solution was made upto 100 m.ls. per litre.

$$\therefore 100 \text{ m.ls. of the solution will contain } \frac{4.48}{10} = 0.448 \text{ gms. per litre of iron.}$$

But 50 m.ls. of the original solution were taken for reduction and made to 100 m.ls.

$\therefore 0.448$ gms. of iron is present in 50 m.ls. of the original ferric salt solution.

$$\therefore \text{amount of iron in 1 litre of the solution} \left\{ \begin{array}{l} = \frac{.448 \times 1000}{50} \\ = 8.96 \text{ gms.} \end{array} \right.$$

4. Calculation of the amount of ferric and ferrous iron in a given solution containing both ferrous and ferric salt.

In this case, a known volume of the given solution is first titrated against standard KMnO_4 , and the strength of iron calculated. This will give amount of ferrous iron in the solution.

A known volume is then reduced as in (3) above and the strength of the iron with solution obtained as described. In this way, the ferric iron will have been converted to the ferrous state and the result obtained will be the total amount of iron present in the solution. Calculate the amount of ferric iron by subtracting the amount of the ferrous iron from the amount of the total iron.

EXAMPLE :—10 m.ls. of a solution containing ferrous and ferric salt required 5 m.ls. of $\frac{N}{10}$ KMnO_4 solution for titration.

50 m.ls. of the solution were then reduced and made upto 250 m.ls. 25 m.ls. of this solution were titrated against $\frac{N}{10}$ KMnO_4 solution and 7.5 m.ls. of the KMnO_4 solution were used. Calculate the amounts of ferrous and ferric iron in the solution.

a. 10 m.ls. of $\frac{N}{x}$ ferrous iron solution ch. = 5 m.ls.

of $\frac{N}{10}$ KMnO_4

$$\therefore 10 \times \frac{N}{x} = 5 \times \frac{N}{10}$$

$$\therefore x = 20.$$

$$\begin{aligned} \therefore \text{strength of ferrous iron} &= \frac{N}{20} \\ &= \frac{56}{20} = 2.8 \text{ gms. per litre.} \end{aligned}$$

$$\begin{aligned} \text{b. } 25 \text{ m.ls. of } \frac{N}{x} \text{ ferrous iron solution ch.} &= 7.5 \text{ m.ls.} \\ &\text{of } \frac{N}{10} \text{KMnO}_4 \end{aligned}$$

$$\therefore 25 \times \frac{N}{x} = 7.5 \times \frac{N}{10}$$

$$\therefore x = \frac{25 \times 10}{7.5} = 30$$

$$\begin{aligned} \therefore \text{strength of the iron solution} &= \frac{N}{30} = \frac{56}{30} = 1.866 \\ &\text{gms. per litre.} \end{aligned}$$

The volume of the solution = 250 m. ls.

$$\begin{aligned} \therefore \text{amount of iron present in 250 m, ls.} &= \\ &= \frac{1.866 \times 250}{1000} = .466 \text{ gm.} \end{aligned}$$

But this volume was obtained from 50 m.ls. of the original solution.

$$\therefore \text{the amount of total iron in 50 m.ls. of the solution} = .466 \text{ gm.}$$

$$\begin{aligned} \therefore \text{amount of total iron in 1 litre} &= \frac{.466 \times 1000}{50} \\ &= 9.32 \text{ gms.} \end{aligned}$$

But amount of ferrous iron in one litre = 2.5 gms.

$$\therefore \text{amount of ferric iron in 1 litre} = 9.32 - 2.5 = 6.8 \text{ gms}$$

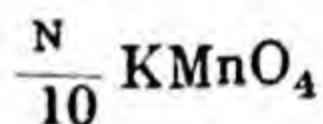
5. Calculation of percentage of impurity in iron wire.

Find out the weight of given iron wire.

Weigh about 1.5 gms. of iron wire, and dissolve it in dilute sulphuric acid in a **Bunsen Valve flask**. When it has completely dissolved, make the solution to a known volume, and titrate against standard KMnO_4 solution and calculate as follows:—

1.5 gms. of iron wire were dissolved in dilute sulphuric acid and the volume made up to 250 m.ls. 25 m.ls. of this solution required 20 m.ls. of $\frac{N}{10}$ KMnO_4 for complete oxidation. Calculate the percentage of impurity in the iron wire.

25 m.ls. of the ferrous solution ch. = 20 m.ls. of



$$\therefore \text{strength of the ferrous iron} = \frac{N}{10} \times \frac{20}{25} = \frac{N}{12.5}$$

$$= \frac{56}{12.5} = 4.48 \text{ gms. per litre}$$

The volume of the solution in which the iron wire was dissolved = 250 m.ls.

$$\therefore \text{amount of iron in 250 m.ls.} = \frac{4.48}{4} = 1.12 \text{ gms.}$$

The wt. of iron wire taken = 1.5 gms.

$$\therefore \text{amount of impurity in 1.5 gms.} = 1.5 - 1.12 = .38 \text{ gm.}$$

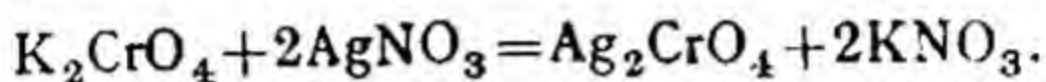
$$\therefore \% \text{age of impurity} = \frac{.38 \times 100}{1.5} = 25.3\%$$

(iii) **Titration involving precipitation.**

When silver titrate solution is added to the solution

of a chloride, a white precipitate is formed.

Hence strengths of the chlorides are determined by titrating them against silver nitrate solutions. The end point is determined by the addition of potassium chromate (K_2CrO_4) solution to the chloride solution. Silver nitrate gives a reddish brown precipitate with a chromate in a neutral solution.



Therefore in such titration, the solution should be neutral. The precipitate of silver chromate is formed only after the whole of the chloride has been precipitated as silver chloride. Hence the end point is reached when a reddish brown precipitate is obtained.

Equivalent Weights :—The equivalent of silver nitrate is 170 and that of chlorine is 35.5. Hence the equivalent weight of a chloride can be easily calculated from the amount of chlorine present in the gram molecule of the substance.

The equivalent weights of substances used in these titrations are as follows :—

$AgNO_3$	=170.
Chlorine	=35.5.
$NaCl$	=58.5.
KCl	=74.5.
$BaCl_2 \cdot 2H_2O$	$= \frac{244}{2} = 122.$
$BaCl_2$ (anhydrous)	=104.
$CaCl_2 \cdot 6H_2O$	$= \frac{219}{2} = 109.5.$
$CaCl_2$ (anhydrous)	=55.5

Examples

1. 25 m.ls. of $\frac{N}{100}$ AgNO_3 were required for 10 m. ls. of sodium chloride solution. Calculate the amount of (i) sodium chloride and (ii) chlorine per litre in the solution.

$$10 \text{ m.ls. of } \frac{N}{x} \text{ NaCl ch.} = 25 \text{ m.ls. of } \frac{N}{100} \text{ AgNO}_3.$$

$$\therefore 10 \times \frac{N}{x} = 25 \times \frac{N}{100}.$$

$$\therefore x = \frac{100 \times 10}{25} = 40$$

$$\text{Hence the strength of NaCl} = \frac{N}{40}$$

$$= \frac{58.5}{40} = 1.46 \text{ gms.}$$

per litre

$$\text{and the amount of chlorine per litre} = \frac{35.5}{40}$$

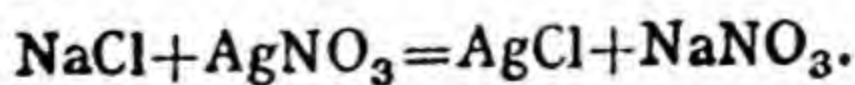
$$= .89 \text{ gm. per litre}$$

2. 1.5 gms. of a mixture of sodium chloride and potassium chloride required 4.218 gms. of silver nitrate to precipitate the whole of chlorine present. Calculate the percentage of each in the mixture.

Let the amount of NaCl in the mixture = x gms.

Then the amount of KCl = $[1.5 - x]$ gms.

With NaCl, the reaction takes place according to the following equation.

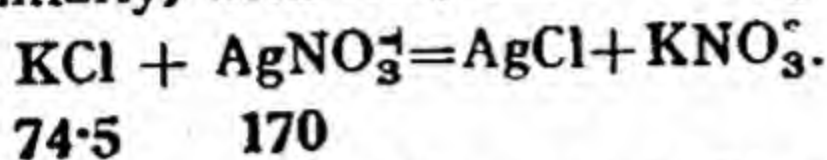


$$58.5 \quad 170$$

So that 58.5 gms. NaCl requires 170 gms. of silver nitrate.

$$\therefore x \text{ gms.} \quad \text{..} \quad \text{..} \quad \frac{x \times 170}{58.5} \text{ gms.} \quad \text{..} \quad \text{nitrate}$$

Similarly, with KCl, the following equation holds



i.e. 74.5 gms. of KCl require 170 gms. of AgNO_3 .

$$\therefore (1.5 - x) \text{ gms.} \quad \text{..} \quad \text{..} \quad = \frac{(1.5 - x) \times 170}{74.5}.$$

Now the total amount of silver nitrate required

$$\frac{170x}{58.5} + \frac{(1.5 - x) \times 170}{74.5} = 4.218 \text{ gms.}$$

$$170 \times 74.5 \times x + 1.5 \times 170 \times 58.5 - 170 \times 58.5 \times x = 4.218 \times 58.5 \times 74.5$$

$$170 \times 74.5 \times x - 170 \times 58.5 \times x = 4.218 \times 58.5 \times 74.5 - 1.5 \times 170 \times 58.5.$$

$$\therefore 2720 x = 18383.1 - 14917.5,$$

$$= 3465.6$$

$$\therefore x = \frac{3465.6}{2720} = 1.275.$$

$$\therefore \text{amount of NaCl in 1.5 gms. of the mixture} = 1.275 \text{ gms.}$$

$$\text{and the amount of KCl} = 1.5 - 1.275 = 0.225 \text{ gm.}$$

$$\therefore \% \text{age of NaCl} = \frac{1.275 \times 100}{1.5} = 85.$$

$$\text{and the \%age of KCl} = 15.$$

3. 10 gms. of Barium Chloride ($\text{BaCl}_2 \cdot x \text{H}_2\text{O}$) were dissolved in one litre of the solution. 10 m.ls. of this solution required 16.5 m.ls. of $\frac{N}{20} \text{AgNO}_3$ for complete precipitation

of the chloride. Calculate the number of molecules of water of crystallisation in the salt.

10 m.ls. of the solution ch. = 16.5 m.ls. of $\frac{N}{20}$ AgNO_3 .

\therefore strength of Barium chloride solution $\frac{N}{20} \times \frac{16.5}{10}$
 $= .0825 \text{ N.}$

The equivalent Wt. of the anhydrous salt = (BaCl_2)
 $= 104.$

\therefore strength of the anhydrous salt = $.0825 \times 104$
 $= 8.58 \text{ gms./litre.}$

The strength of the hydrogen salt = 10 gms. per litre.

\therefore the amount of water in 10 gms. of the crystals
 $= 10 - 8.58 = 1.42.$

So that 8.52 gms. of the anhydrous salt
 combines with 1.48 gms. of water of crystallisation.

\therefore 208 gms. will combine with = $\frac{1.48 \times 208}{8.52}$
 $= 36.1 \text{ gms. of water.}$

\therefore the number of molecules of
 water of crystallisation $\left\{ = \frac{36.1}{18} = 2 \text{ Ans.} \right.$

4. 5 gms. of a mixture of sodium chloride and sodium sulphate were dissolved in one litre. 20 m.ls. of this solution required 50 m.ls. of $\frac{N}{50}$ AgNO_3 for complete precipitation of the chloride. Calculate the percentage composition of the mixture.

In this case, only the chloride is acted upon by silver nitrate and the sodium sulphate is inactive. So from the titration data, we can find out the strength of sodium chloride.

$$50 \text{ m.l.s. of } \frac{N}{50} \text{ AgNO}_3 \text{ ch.} = 20 \text{ m. l.s. of } \frac{N}{x} \text{ NaCl}$$

$$\therefore 50 \times \frac{N}{50} = 20 \times \frac{N}{x}$$

$$\therefore x = 20.$$

$$\begin{aligned} \therefore \text{strength of sodium chloride} &= \frac{N}{20} \\ &= \frac{58.5}{20} = 2.925 \text{ gms.} \\ &\quad \text{per litre.} \end{aligned}$$

$$\begin{aligned} \text{The amount of NaCl in 5 gms. of the mixture} \\ &= 2.925 \text{ gms.} \end{aligned}$$

$$\begin{aligned} \text{Hence the amount Na}_2\text{SO}_4 \text{ in 5 gms. of the mixture} \\ &= 5 - 2.925 \\ &= 2.075 \text{ gms.} \end{aligned}$$

$$\therefore \% \text{age of NaCl} = \frac{2.925 \times 100}{5} = 58.5$$

$$\text{and the \%age of Na}_2\text{SO}_4 = \frac{2.075 \times 100}{5} = 41.5$$

EXERCISES

1. What volume of $\frac{N}{10}$ -HCl will be required to neutralize 25 m.ls. of $\frac{N}{17}$ Na_2CO_3 solution?
2. How much sodium hydroxide will be required in order to neutralise 20 m.ls. of normal sulphuric acid?
3. 5 gms. of sulphuric acid required 850 m.ls. of $\frac{N}{10}$ caustic soda for complete neutralisation. Calculate the strength of the acid.
4. By Kjeldahl's method, 1.256 gms. of an organic substance gave ammonia that require 30 m.ls. of $\frac{N}{20}$ H_2SO_4 for neutralisation. Calculate the percentage of nitrogen in the substance.
5. 0.5278 gm. of an organic substance, on being Kjeldahlised gave ammonia that was passed into 50 m.ls. of normal acid. The excess of the acid required 34 m.ls. of normal caustic soda for complete neutralisation. Calculate the percentage of nitrogen in the substance.
6. How would you determine, volumetrically, the number of molecules of water of crystallisation in oxalic acid.
7. 25 m.ls. of a ferrous sulphate solution required 10 m.ls. of N. KMnO_4 for oxidation. Calculate the amount of iron per litre of the solution.
8. A solution of 0.980 gm. of an iron are required 50 m.ls. of potassium permanganate solution containing 1.5 gms. of the salt per litre. Calculate the percentage of

9. Describe the method for determining the number of molecules of water of crystallisation in Barium chloride ($\text{BaCl}_2 \cdot x\text{H}_2\text{O}$), volumetrically.

10. 10 gms. of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ are required to neutralize 50 m.l.s. of a solution of HCl . How many m.l.s. of the acid must be diluted and made up to one litre in order that we may get a neutral solution of HCl ?

11. To 50 m.l.s. of a solution of HCl , 25 m.l.s. of a 82 N. NaOH solution were added. The excess of the acid in the solution required 30 m.l.s. of a .09N. Na_2CO_3 solution for neutralization. Find out the normality of the acid solution and the strength of the acid per litre.

12. .5 gm. of pure CaCO_3 was to require 47 m.l.s. of dilute HCl for complete neutralization. Find the normality of the acid.

13. In Kjeldahl's nitrogen estimation, the ammonia resulting from .1475 gm. of the substance was distilled into 50 m.l.s. of $\frac{N}{10}$ HCl and the excess of the acid required 25 m.l.s. of $\frac{N}{10}$ alkali for exact neutralization. Calculate the percentage of nitrogen in the substance.

14. Describe how you will find the percentage of each in a solution, containing sodium carbonate and sodium bicarbonate.

15. 0.125 gm. of a sample of impure limestone was dissolved in 30 m.l.s. of $N/10$ HCl , and the solution was then made up to 100 m.l.s., 10 m.l.s. of the diluted solution required for complete neutralization, 15 m.l.s. of $N/20$ NaOH solution. Calculate the percentage of calcium carbonate in limestone.

[U. P. Board Inter 1948]

16. 20 m.l.s. of a solution of a mono acid base requir-

ed for neutralisation 10 m. ls. of an acid solution. The two solutions are equi-molar. What is the basicity of the acid?

[*Delhi Inter. 1939*].

17. You are given a mixture of Na_2CO_3 and Na_2SO_4 containing 53% of Na_2CO_3 . If 5 gms. of the mixture are dissolved and made up 500 m.ls. with distilled water and 50 m.ls. pipette is supplied. What volume of decinormal acid will neutralize one pipette full.

[*U. P. Board Inter 1946*].

18. 200 m.ls. H_2SO_4 solution of unknown strength is found to contain as much acid as 30 m.ls. of H_2SO_4 solution containing 5 gms. per litre. Calculate the strength of unknown H_2SO_4 in terms of normality and gms. per litre.

[*Delhi Inter 1928*]

19. 5 m.ls. of strong H_2SO_4 are diluted with water and the volume made up to 500 m.ls. Upon titration 10.2 m.ls. of this diluted acid is found to neutralize exactly 22.7 m.ls. of N/10 Na_2CO_3 solution. What volume of water must be added to 400 m.ls. of the diluted acid to make it exactly decinormal?

[*U. P. Board Inter Agri. 1942*]

20. Calculate the percentage strength of H_2SO_4 in a sample of the acid from the following data: the sp. gr. of the acid is 1.76: 3.5 m.ls. of the acid were diluted to one litre; and 25 m.ls. of the dilute acid neutralised 24.3 m.ls. of N/10 NaOH solution.

[*U. P. Board Inter. 1932*]

21. 3.172 grams of sodium carbonate crystals were weighed out, dissolved in water, and made up to 250 m ls. Three successive samples of 25 m.ls. of this solution required 28.05 m.ls., 27.90 m.ls. and 27.90 m.ls. respec-

tively for titration with $\cdot 93$ N/10 H_2SO_4 , using methyl orange as indicator. Calculate the percentage of Na_2CO_3 in the crystals.

[U. P. Board Inter Agri. 1940]

22. Calculate the percentage of calcium carbonate in a sample of limestone from the following data : 0.125 gm. of limestone was dissolved in 30 m.ls N/10 HCl and the solution boiled. The solution required 1.5 m ls. of N/2 caustic soda solution for neutralisation.

[U. P. Board Inter. 1932.]

23. What volume of NH_3 at N. T. P. will be required to neutralize a solution of HCl containing 0.5 gm. of HCl ?

[Patna Inter. Science]

24. How many m.ls. of N/10 sodium hydroxide solution would be required to completely neutralize 0.122 gm. benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)?

[Punjab Inter. 1940.]

25. 100 gms. of HCl solution of specific gravity 1.17 contains 33.4 gms. of HCl . How many litres of the acid solution of this strength would be required to neutralize 5 litres of the decinormal solution of Caustic Soda.

[U. P. Board Inter. 1942]

26. 0.2815 gm. of CaCO_3 is dissolved in 30 m.ls. of normal HNO_3 solution. The excess of acid requires 24.43 m.ls. N- NaOH solution. Calculate the percentage of CO_2 in the sample of CaCO_3 .

[U. P. Board. Inter 1928]

27. A quantity of ammonium chloride is boiled with 100 m.ls. of 0.8 N. NaOH solution until no further chemical change takes place. It is then found that excess of NaOH requires 12.5 m.ls. of 0.75 N. H_2SO_4 to

neutralize it. How much Ammonium chloride was taken?

28. 0.72 gram of a metal required 22.2 m.ls. of Normal HCl to dissolve it. What is the equivalent weight of the metal?

29. 10 gms. of sodium hydroxide which is 95% pure is dissolved in 200 m.ls. water. Then 50 m.ls. of 1.5 N HCl is mixed with the above solution and the whole diluted to exactly 500 m.ls. Calculate the acidity or alkalinity of the resultant diluted mixture in terms of normality.

[Calcutta Inter. and U. P. Inter., Agri. 1944.]

30. One gm. of the carbonate of a metal was dissolved in 25 m.ls. normal HCl. The resulting liquid required 50 m.ls. N/10 caustic soda solution to neutralize it completely. Calculate the eqvt. weight of the carbonate.

[U. P. Board. Inter 1947]

PART II ORGANIC

CHAPTER XII

PERCENTAGE COMPOSITION

Determination of the percentages of different elements present in an organic compound.

The percentage of elements in organic compounds is very important in the study of the composition of such compounds. Different elements are estimated by different methods and the percentage of each element so obtained is used for the determination of the formula of the compound.

The following elements are estimated in connection with organic analysis.

Carbon, hydrogen, nitrogen, halogens, sulphur and phosphorus. (*For details of their estimation see Intermediate Organic Chemistry by the authors.*) **Oxygen is always estimated by difference.**

(a) **Carbon and hydrogen** :—Carbon and hydrogen are estimated by heating a known weight of the substance in a combustion tube containing copper oxide. The tube is heated in a combustion furnace. The carbon and hydrogen present in the substance get oxidised into carbon dioxide and water. The water formed is absorbed in a weighed caustic potash bulbs. The increase in weight in the calcium chloride tube represents the amount of water formed and that in the potash bulbs represents the weight of carbon dioxide formed.

From the weights of water and carbon dioxide formed, the weights of hydrogen and carbon are calculated as follows:—

Carbon dioxide has the formula CO_2 .

Now its molecular weight will be $12+32=44$.

So that 44 gms. of CO_2 contains 12 gms. of carbon.

Now if x gms. of carbon dioxide is formed.

The Wt. of carbon in it $= \frac{12 \times x}{44}$ gms.

From this the percentage of carbon can be calculated. In the case of water, H_2O , we find that the molecular weight is $2+16=18$

and 18 gms. of water contain 2 gms. of hydrogen. Therefore if the Wt. of water obtained is y gms. it will contain $\frac{2 \times y}{18}$ gms. of hydrogen.

From this weight the percentage of hydrogen can be calculated.

EXAPMLE 1. *0.21471 gm. of a substance gave 0.4391 gms carbon dioxide and 0.7830 gm. water. Calculate the percentage of carbon and hydrogen in the compound.*

Wt. of $\text{CO}_2 = 0.4391$ gm.

44 gms. of carbon dioxide contain 12 gms. of carbon

$\therefore 0.4391$ gm. of carbon oxide will contain

$$\frac{0.4391 \times 12}{44} \text{ gms. of carbon}$$

Wt. of the substance taken $= 0.21471$ gm.

$$\therefore \text{percentage of carbon} = \frac{0.4391 \times 12}{44} \times \frac{100}{0.21471} = 55.7.$$

Wt. of water formed $= 0.7830$ gm.

Now 18 gms. of water contains 2 gms. of hydrogen.

$$\therefore 0.783 \text{ gm. of water contains} = \frac{0.783 \times 2}{18} = 0.087 \text{ gm. of hydrogen}$$

Wt. of the substance taken = 2.1471 gm.

$$\therefore \text{percentage of hydrogen} = \frac{0.087 \times 100}{2.1471} = 40.5.$$

$$\therefore \text{percentage of carbon} = 55.7.$$

and percentage of hydrogen = 40.5.

EXAMPLE 2. 0.306 gm. of an organic substance gave on combustion 0.900 gm. of carbon dioxide and 0.304 gm. of water. Calculate the percentage of carbon and hydrogen in the compound.

Wt. of carbon dioxide formed = 0.9 gm.

$$\therefore \text{Wt. of carbon present} = \frac{0.9 \times 12}{44} \text{ gm.}$$

Wt. of the substance = 0.306 gm.

$$\therefore \text{the percentage of carbon} = \frac{0.9 \times 12}{44} \times \frac{100}{0.306} = \frac{90}{1.122} = 80.2$$

Wt. of water formed = 0.304 gm.

$$\text{Wt. of hydrogen present} = \frac{0.304}{9} \text{ gms.}$$

$$\text{Hence the \%age of hydrogen} = \frac{0.304}{9} \times \frac{100}{0.306} = 11.40$$

EXAMPLE 3. An organic substance, containing carbon, hydrogen and oxygen gave the following data on combustion.

0.20 gm. gave 0.195 gm. of CO_2 and 0.040 gm. of water. Find out the percentage composition of the compound.

Wt. of the substance = 0.20 gm.

Wt. of CO_2 formed = 0.195 gm.

$$\therefore \text{Wt. of carbon present} = \frac{.195 \times 12}{44} \text{ gm.}$$

$$\begin{aligned} \text{Hence the percentage of carbon} &= \frac{.195 \times 12}{44} \times \frac{100}{.2} \\ &= 26.5 \end{aligned}$$

$$\text{Wt. of water formed} = .040 \text{ gm.}$$

$$\therefore \text{Wt. of hydrogen present} = \frac{.04}{9} \text{ gm.}$$

$$\text{Hence the \%age of hydrogen} = \frac{.04}{9} \times \frac{100}{.2} = 2.2$$

The substance also contains oxygen, the percentage of which can be obtained by difference.

$$\begin{aligned} \therefore \text{The percentage of oxygen} &= 100 - (26.5 + 2.2) \\ &= 100 - 28.7 = 71.3. \end{aligned}$$

Therefore the percentage composition of the substance is.

$$C = 26.5\%$$

$$H = 2.2\%$$

$$O = 71.3\%$$

(b) Nitrogen. Nitrogen inorganic compounds is estimated by Duma's method and Kjeldahl's method.

In the Duma's method the nitrogenous organic substance is mixed with cupric oxide and heated in a combustion tube, in an atmosphere of carbon dioxide. [For details of the arrangement in the combustion tube, see Organic Chemistry].

The nitrogen present in the compound is collected over caustic potash in a nitrometer and its volume is recorded.

The volume so obtained is calculated at N.T.P. and the Wt. of nitrogen is obtained and the percentage calculated.

N.B.—1 m.l. of nitrogen at N.T.P. has the weight = 0.00126 gm.

Or 22.4 litres (22400 m.ls.) of nitrogen at N.T.P. weigh = 28 gms.

EXAMPLE 4. 0.3183 gm. of a substance gave 42 m.ls. of dry nitrogen at 17°C and 764 mm. pressure. Calculate the percentage of nitrogen in the compound.

Volume of nitrogen = 42 m.ls.

Temperature = 17 + 273 = 290° absolute.

Pressure = 764 mm.

Now volume at N.T.P. has got to be obtained

∴ applying the equation $\frac{PV}{T} = \frac{P_1V_1}{T_1}$; we get

$$\frac{42 \times 764}{290} = \frac{x \times 760}{273} \quad \text{Where } x \text{ stands for volume at N.T.P.}$$

$$\begin{aligned} \therefore x &= \frac{42 \times 273 \times 764}{290 \times 760} \text{ m.ls.} \\ &= 39.75 \text{ m.ls.} \end{aligned}$$

∴ volume of N₂ at N.T.P. = 39.75 m.ls.

∴ the Wt. of N₂ = 39.75 × 0.00126 gm.

$$\therefore \% \text{age of N}_2 = \frac{39.75 \times 0.00126 \times 100}{0.3183} = 15.7$$

EXAMPLE 5. An organic compound containing carbon, hydrogen, nitrogen and oxygen gave on analysis the following results :—

0.2501 gm. gave 0.3862 gm. of CO₂ and

0.0517 gm. H₂O.

11.61 gms. gave 13.5 m.ls. of nitrogen at 18°C and 755 mm. pressure. Calculate the percentage composition of the compound.

(i) Wt. of the substance = 0.2501 gm.

Wt. of CO_2 formed = 0.3862 gm.

$$\therefore \text{Wt. of carbon present} = \frac{0.3862 \times 12}{44} \text{ gm.}$$

$$\begin{aligned} \text{Hence \%age of carbon} &= \frac{0.3862 \times 12}{44} \times \frac{100}{0.2501} \\ &= 42.1 \end{aligned}$$

(ii) Wt. of water formed = 0.0517 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{0.0517}{9} \text{ gm.}$$

$$\begin{aligned} \text{Hence \%age of hydrogen} &= \frac{0.0517}{9} \times \frac{100}{0.2501} \\ &= 22.7 \end{aligned}$$

(iii) Volume of N_2 obtained = 13.5 m.ls.

Temperature = $273 + 18 = 291^\circ \text{A.}$

Pressure = 755 mm.

$$\therefore \text{volume at N.T.P.} = \frac{13.5 \times 755 \times 273}{291 \times 760} \text{ m.ls.}$$

Wt. of 1 m.l. of N_2 = 0.00126 gm.

$$\therefore \text{Wt. of nitrogen so obtained} = \frac{13.5 \times 755 \times 273}{291 \times 760} \times 0.00126 \text{ gm.}$$

$$\begin{aligned} \text{Hence percentage of } \text{N}_2 &= \frac{13.5 \times 755 \times 273}{291 \times 760} \times 0.00126 \\ &\quad \times \frac{100}{0.2501} = 12.8 \end{aligned}$$

(iv) Percentage of C = 42.1.

„ „ H = 2.27

„ „ N = 12.8

$$\therefore \% \text{age of oxygen} = 100 - (42.1 + 2.27 + 12.8)$$

$$\begin{aligned} (\text{By difference}) &= 100 - 57.17 \\ &= 42.83 \end{aligned}$$

EXAMPLE 6. 0.2825 gm. of an organic substance gave on combustion 11.53 m.ls. of nitrogen collected over water at 15°C. and 773 mm. pressure. Calculate the percentage of nitrogen (Aq. Tension = 12.17 mm.).

Volume of N_2 = 11.53 m.ls.

Temperature = $273 + 15 = 288^\circ A.$

Pressure = 773 mm.

Aq. Tension = 12.7 mm.

\therefore Actual pressure of the gas = $773 - 12.7 = 760.3$ mm.

Volume at N.T.P. = $\frac{11.53 \times 760.3 \times 273}{760 \times 288}$ m.ls.
= 10.93 m.ls.

Wt. of 1 m.l. nitrogen = 0.00126 gm.

\therefore „ 10.93 „ = 10.93×0.00126 gm.

Wt. of the substance taken = 0.2825 gm.

\therefore %age of nitrogen = $\frac{10.93 \times 0.00126 \times 100}{0.2825} = 4.9$

(b) **Kjeldahl's Method.** This method consists in heating the nitrogenous substance with concentrated sulphuric acid and some potassium sulphate and cupric sulphate which serve to facilitate the oxidation of the substance with sulphuric acid. The nitrogen in the substance is thus converted into ammonium sulphate. This is heated with excess of caustic soda. The ammonia evolved.

$(NH_4)_2 SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$ is passed into a known volume of a standard solution of an acid. The acid is neutralized by the ammonia and the strength of the residual acid is determined by titration against standard alkali. From the amount of the acid used; the amount of ammonia is calculated and from this the amount of nitrogen present in the known weight of the substance is calculated.

EXAMPLE 7. In a Kjeldahl nitrogen estimation the ammonia resulting from 0.442 gm. of the substance was dis-

titled into 50 m.ls. of $\frac{N}{10} \text{H}_2\text{SO}_4$. The excess of the acid required 14.0 m.ls. of $\frac{N}{10} \text{NaOH}$. Calculate the percentage of nitrogen in the substance.

14.0 m.ls. of $\frac{N}{10} \text{NaOH}$ are equivalent to 14 m.ls. of $\frac{N}{10} \text{H}_2\text{SO}_4$

\therefore volume of $\frac{N}{10} \text{H}_2\text{SO}_4$ neutralized by ammonia that is evolved = $50 - 14 = 36$ m.ls.

36 m.ls. of $\frac{N}{10} \text{H}_2\text{SO}_4 = 36$ m.ls. of $\frac{N}{10} \text{NH}_4\text{OH}$.

Now the amount of combined nitrogen contained in 1 litre of normal $\text{NH}_4\text{OH} = 14$ gms.

\therefore Amount of nitrogen contained in 36 m.ls. of $\frac{N}{10} \text{NH}_4\text{OH} = 14 \times \frac{36}{1000} \times \frac{1}{10} = 0.0504$ gm.

Hence the percentage of nitrogen in the substance

$$= \frac{0.0504 \times 100}{0.442} = 11.4 \text{ percent}$$

EXAMPLE 8. 0.3465 gm. of a substance containing nitrogen was heated with cone. H_2SO_4 , the product distilled with excess of Caustic Soda and the evolved ammonia absorbed in 50 m.ls. of $\text{N.H}_2\text{SO}_4$. This was diluted to 1000 m.ls. and 25 m.ls. of this solution required 11.43 m.ls. of $\frac{N}{10} \text{NaOH}$ for neutralization. Calculate the percentage of nitrogen.

25 m.ls. of acid require 11.43 m.ls. of $\frac{N}{10} \text{NaOH}$

1000 „ „ „ „ $\frac{11.43 \times 1000}{25} = 457.2$ m.ls.

$\frac{N}{10} \text{NaOH}$

Since this volume of NaOH is equivalent to the unsued acid.

$$457.2 \text{ m.l.s. of } \frac{N}{10} \text{ NaOH} = 45.72 \text{ m.l.s. of N. H}_2\text{SO}_4$$

$$\begin{aligned} \therefore \text{Vol. of N. H}_2\text{SO}_4 \text{ neutralised by ammonia} \\ = 50 - 45.72 \\ = 4.28 \text{ m.l.s.} \end{aligned}$$

1000 m.l.s. of N. H₂SO₄ are equivalent to 17 gms. of ammonia.

$$\begin{aligned} \therefore 4.28 \text{ m.l.s. N. H}_2\text{SO}_4 \text{ are equivalent to} \\ \frac{17 \times 4.28}{1000} \text{ gms. of ammonia.} \end{aligned}$$

Wt. of nitrogen in 0.3465 gm. of the substance

$$= \frac{17 \times 4.28}{1000} \times \frac{14}{17}$$

$$\begin{aligned} \therefore \text{percentage of nitrogen} &= \frac{17 \times 4.28}{1000} \times \frac{14}{17} \times \frac{100}{0.3465} \\ &= 17.3 \end{aligned}$$

(c) Halogens, Sulphur and phosphorus. These elements are estimated by Carius method. (For details see Organic Chemistry :—

(i) In the case of the halogens, a known weight of the substance is heated in presence of fuming nitric acid and silver nitrate crystals in a Carius' tube. The halogen present in the substance is converted into the corresponding silver halide, AgCl, AgBr or AgI. The silver halide is dried and weighed. From this the percentage of the halogen is calculated as follows:—

Suppose x gms. of the substance gives y gms. of silver chloride, AgCl.

From the formula AgCl, we find that

$(108 + 35.5) = 143.5$ gms. of silver chloride contain 35.5 gms. of chlorine.

$\therefore y$ gms. of the salt will contain $\frac{y \times 35.5}{143.5}$ of chlorine,

\therefore The percentage of chlorine = $\frac{y \times 35.5}{143.5} \times \frac{100}{x}$

Similarly, in the case of AgBr, 188 gms. of silver
108 + 80

Bromide contain 80 gms. of Bromine. Therefore y gms. of the silver Bromide will contain $\frac{80 \times y}{188}$ gms. of Bromine, from which the percentage can be calculated as above.

In the case of AgI, 235 gms. of the iodide
108 + 127
contain 127 gms. of iodine, therefore y gms. of silver iodide will contain $\frac{y \times 127}{235}$ gms. of iodine.

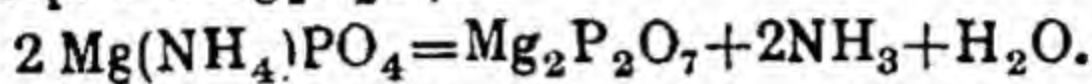
The percentage can be calculated as above.

(ii) When sulphur is to be estimated, the sulphur present in the substance is oxidised to sulphuric acid, which is treated with Barium chloride when Barium sulphate, BaSO_4 , is precipitated. It is filtered, dried and weighed.

From the formula Ba SO_4 we find that
 $137 + 32 + 64 = 233$

233 gms. of Barium sulphate contains 32 gms. of sulphur
Therefore if y gms. of Barium sulphate are formed, then it will contain $\frac{32 \times y}{233}$ gms. of sulphur, from which its percentage can be calculated.

(iii) In the case of the estimation of phosphorus, it is converted in the Carius tube into phosphoric acid H_3PO_4 , which, when treated with magnesia mixture, gives a precipitate of magnesium ammonium phosphate $\text{Mg}(\text{NH}_4)\text{PO}_4$, which is dried and ignited over a blow-pipe flame, when it is converted into magnesium pyrophosphate $\text{Mg}_2\text{P}_2\text{O}_7$.



Magnesium pyrophosphate is weighed, and the percentage of phosphorus is calculated from it as follows

From the formula, $\text{Mg}_2\text{P}_2\text{O}_7$, we find that

$$\begin{aligned} & 2 \times 24 + 2 \times 31 + 7 \times 16 \\ & = 48 + 62 + 112 = 222 \end{aligned}$$

222 gms. of the salt contain 62 gms. of phosphorus. So that if y gms. of the salt are formed, the wt. of phosphorus

$$= \frac{y \times 62}{222} \text{ gms.}$$

From this weight, the percentage of phosphorus can be calculated.

EXAMPLE 9. *0.2325 gm. of an organic substance on being treated by Carius' method, gave 0.3505 gm. of silver chloride. Calculate the percentage of chloride in the substance.*

Wt. of silver chloride = 0.3505 gm.

Now 143.5 gms. of silver chloride AgCl contain
(108 + 35.5 = 143.5)

35.5 gms. of chlorine.

\therefore 0.3505 gm. of silver chloride contain

$$\begin{aligned} & \frac{0.3505 \times 35.5}{143.5} \text{ gms.} \\ & = 0.0867 \text{ gm.} \end{aligned}$$

Wt. of the substance = 0.2325 gm.

$$\therefore \text{percentage of chlorine} = \frac{100 \times 0.0867}{0.2325} = 37.3.$$

EXAMPLE 10. 0.5036 gm. of a substance gave .5276 gm. of BaSO_4 . Calculate the percentage of sulphur in the substance.

Wt. of BaSO_4 formed = .5276 gm.

From the formula BaSO_4 , we find that 233 gms.
(137 + 32 + 64 = 233)

of the salt contain 32 gms. of sulphur.

$$\therefore \text{Wt. of sulphur in } .5276 \text{ gm. of } \text{BaSO}_4 = \frac{32 \times .5276}{233} \text{ gm.}$$

The Wt. of the substance taken = .5036 gm.

$$\therefore \text{percentage of sulphur in the substance} = \frac{32 \times .5227}{233} \times \frac{100}{.5036} = 14.4.$$

EXAMPLE 11. 0.215 gm. of a substance gave 0.195 gm. of silver iodide. Calculate the percentage of iodine in the compound.

Wt. of silver iodide formed = .195 gm.

From the formula AgI , we find that 235 gm.
(108 + 127 = 235)

of silver iodide contain 127 gms. of iodine.

$$\therefore \text{Wt. of iodine in } .195 \text{ gm. of silver iodide} = \frac{.195 \times 127}{235} \text{ gm.}$$

Wt. of the substance taken = .215 gm.

$$\therefore \text{percentage of iodine} = \frac{.195 \times 127}{235} \times \frac{100}{.215} = 49.01.$$

EXAMPLE 12, .9360 gm. of an organic compound gave

1.542 gms. of magnesium pyrophosphate. Calculate the percentage of phosphorus in the compound.

Wt. of magnesium pyrophosphate formed = 1.542 gms.

From the formula $\text{Mg}_2\text{P}_2\text{O}_7$, we find, that
(48 + 62 + 112 = 222)

222 gms. of the substance contain 62 gms. of phosphorus.

\therefore Wt. of phosphorus present in 1.542 gms. of the

$$\text{phosphate} = \frac{1.542 \times 62}{222} \text{ gm.}$$

Wt. of the substance taken = .936 gm.

$$\therefore \text{percentage of phosphorus} = \frac{1.542 \times 62}{222} \times \frac{100}{.936} = 48.3.$$

(d) Miscellaneous.

EXAMPLE 13. 0.152 gm. of a substance on combustion gave 0.304 gm. CO_2 and 0.124 gm. H_2O . Calculate the percentage composition of the substance.

[i] Wt. of CO_2 = .304 gm.

$$\therefore \text{Wt. of carbon present} = \frac{.304 \times 12}{44} \text{ gm.}$$

Wt. of the substance = .152 gm.

$$\begin{aligned} \therefore \text{percentage of carbon} &= \frac{.304 \times 12}{44} \times \frac{100}{.152} \\ &= \frac{600}{11} = 54.55. \end{aligned}$$

(ii) Wt. of H_2O = .124 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{.124}{9} \text{ gm.}$$

$$\therefore \text{percentage of hydrogen} = \frac{.124}{9} \times \frac{10}{.152}$$

$$= \frac{12400}{1368} = 9.06$$

(iii) Percentage of oxygen [by difference]

$$= 100 - [54.55 + 9.06]$$

$$= 100 - 63.61 = 36.39.$$

$$\therefore C = 54.55\%$$

$$H = 9.06\%$$

$$O = 36.39\%$$

EXAMPLE 12. *The analysis of an organic compound gave the following data:—*

0.4260 gm. gave 0.288 gm. CO_2 and 0.0886 gm. H_2O . 0.2130 gm. gave 0.4703 gm. $AgCl$. Calculate the percentage composition of the compound.

(i) Wt. of the substance taken = 0.4260 gm.

Wt. of CO_2 formed = 0.288 gm.

$$\therefore \text{Wt. of carbon present} = \frac{.288 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon in the compound} = \frac{.288 \times 12}{44}$$

$$\times \frac{100}{.4260} = 18.5,$$

(ii) Wt. of the substance taken = 0.426 gm.

Wt. of water formed = 0.0886 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{.0886}{9} \text{ gm.}$$

$$\therefore \text{percentage of hydrogen} = \frac{.0886}{9} \times \frac{100}{.4260} = 2.3.$$

(iii) Wt. of the substance taken = 0.2130 gm.

Wt. of AgCl formed = 0.4703 gm.

$$\therefore \text{Wt. of chlorine present} = \frac{0.4703 \times 35.5}{143.5} \text{ gm.}$$

$$\therefore \% \text{ age of chlorine} = \frac{0.4703 \times 35.5}{143.5} \times \frac{100}{0.213} = 54.6$$

(iv) As the sum of the percentages is less than 100, the compound contains oxygen as well.

$$\begin{aligned} \therefore \% \text{ age of oxygen (by difference)} \\ &= 100 - (18.5 + 2.3 + 54.6) \\ &= 100 - 75.4 = 24.6. \end{aligned}$$

$$\therefore \text{C} = 18.5 \%$$

$$\text{H} = 2.3 \%$$

$$\text{Cl} = 54.6 \%$$

$$\text{O} = 24.6 \%$$

EXAMPLE 15.0.184 gm. of a substance gave 0.193 gm. CO_2 and 0.069 gm. water. 0.2141 gm. gave 0.2410 gm. of silver bromide. Calculate the percentage composition of the substance.

(i) Wt. of the substance taken = 0.184 gm.

Wt. of CO_2 formed = 0.193 gm.

$$\therefore \text{Wt. of carbon present} = \frac{0.193 \times 12}{44} \text{ gm.}$$

$$\begin{aligned} \therefore \% \text{ age of carbon in the substance} &= \frac{0.193 \times 12}{44} \times \\ &\quad \frac{100}{0.184} = 27.9 \\ &= 27.9 \end{aligned}$$

(ii) Wt. of the substance taken = 0.184 gm.

Wt. of H_2O formed = 0.069 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{.069}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{.069}{9} \times \frac{100}{.184} = 4.1.$$

(iii) Wt. of the substance taken = .2141 gm.

$$\text{Wt. of AgBr formed} = .241 \text{ gm.} \left[\begin{array}{l} \text{AgBr.} \\ (108 + 80 = 188). \end{array} \right.$$

$$\therefore \text{Wt. of Bromine present} = \frac{.241 \times 80}{188} \text{ gm.}$$

$$\therefore \% \text{age of Bromine} = \frac{.241 \times 80}{188} \times \frac{100}{.2141} = 47.9.$$

(iv) The percentage of oxygen (by difference)

$$\begin{aligned} &= 100 - (27.9 + 4.1 + 47.9) \\ &= 100 - 79.9 = 20.1. \end{aligned}$$

$$\therefore \text{C} = 27.9 \%$$

$$\text{H} = 4.1\%$$

$$\text{Br} = 47.9\%$$

$$\text{O} = 20.1\%$$

EXAMPLE 16. 0.3114 gm. of an organic substance gave 0.8061 gm. CO_2 and 0.2230 gm. H_2O , and 0.2825 gm. of the substance gave 11.53 m.l.s. of nitrogen collected over water at 15°C . and 773 mm. pressure. Calculate the percentage composition of the substance. (Aqueous Tension at $15^\circ\text{C} = 12.7 \text{ mm.}$)

(i) Wt. of the substance taken = .3114 gm.

$$\text{Wt. of } \text{CO}_2 \text{ formed} = .8061 \text{ gm.}$$

$$\therefore \text{Wt. of carbon present} = \frac{.8061 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon in the substance} = \frac{.8061 \times 12}{44}$$

$$\times \frac{100}{.3114} = 70.59$$

(ii) Wt. of the substance taken = 0.3114 gm.

Wt. of H_2O formed = 0.223 gm.

\therefore Wt. of hydrogen in the substance = $\frac{0.223}{9}$ gm.

\therefore %age of hydrogen in the substance = $\frac{0.223 \times 100}{9 \times 0.3114}$
= 7.93

(iii) Wt. of the substance taken = 0.2825 gm.

Vol. of nitrogen collected = 11.53 m.ls.

Temperature = $273 + 15 = 288^\circ A$.

Pressure = $773 - 12.7 = 760.3$ mm.

\therefore volume at N.T.P. = $\frac{11.53 \times 760.3 \times 273}{760 \times 282}$
= 10.93 m.ls.

Wt. of nitrogen collected = 10.93×0.00126 gm.

Hence the percentage of nitrogen in the substance

$$= \frac{10.93 \times 0.00126 \times 100}{0.2825} = 4.91$$

(iv) The percentage of oxygen (by difference)

$$= 100 - (70.59 + 7.93 + 4.91)$$

$$= 100 - 83.43 = 16.57$$

$$\therefore C = 70.59\%$$

$$H = 7.93\%$$

$$N = 4.91\%$$

$$O = 16.57\%$$

EXAMPLE 17. 0.2965 gm. of an organic substance gave 0.8697 gm. CO_2 and 0.1779 gm. water.

0.1965 gm. of the substance gave 22.25 m.ls. nitrogen (dry) at $18^\circ C$ and 763 mm. pressure. Calculate the percentage composition of the substance.

(i) Wt. of the substance taken = .2965 gm.

Wt. of CO_2 formed = .8697 gm.

\therefore Wt. of carbon present = $\frac{.8697 \times 12}{44}$ gm.

\therefore %age of carbon in the sub. = $\frac{.8697 \times 12}{44} \times \frac{100}{.2965}$
= 79.99

(ii) Wt. of substance taken = .2965 gm.

Wt. of water formed = .1779 gm.

\therefore Wt. of hydrogen present = $\frac{.1779}{9}$ gm.

\therefore %age of hydrogen in the Subs. = $\frac{.1779}{9} \times \frac{100}{.2965}$
= 6.66.

[iii] Wt. of the substance taken = .1965 gm.

Vol. of nitrogen collected = 22.25 m.ls.

Temperature = $18 + 273 = 291^\circ \text{A.}$

Pressure = 763 mm.

\therefore Volume of nitrogen at N.T.P.

$$= \frac{22.25 \times 763 \times 273}{760 \times 291} \text{ m.ls.}$$

\therefore Wt. of nitrogen collected

$$= \frac{22.25 \times 763 \times 273 \times .00126}{760 \times 291} \text{ gm.}$$

\therefore %age of nitrogen = $\frac{22.25 \times 763 \times 273 \times .00126}{760 \times 291}$

$$\times \frac{100}{1965} = 13.35.$$

$$C=79.99\%$$

$$H=6.66\%$$

$$N=13.35\%$$

$$100\%$$

EXAMPLE 18. An organic compound gave on analysis the following results:—

0.1348 gm. gave 0.322 gm. CO_2 and 0.662 gm. H_2O .
0.1564 gm. gave 0.774 gm. $BaSO_4$. Calculate the percentage composition of the substance.

(i) Wt. of the substance taken = 0.1348 gm.

Wt. of CO_2 formed = 0.322 gm.

$$\therefore \text{Wt. of carbon present} = \frac{0.322 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon in the substance} = \frac{0.322 \times 12}{44} \times \frac{100}{0.1348} = 65.82$$

(ii) Wt. of the substance taken = 0.1348 gm.

Wt. of H_2O formed = 0.662 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{0.662}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen in the substance} = \frac{0.662}{9} \times \frac{100}{0.1348} = 5.45$$

(iii) Wt. of the substance taken = 0.1564 gm.

Wt. of $BaSO_4$ formed = 0.774 gm.

$$BaSO_4 = (137 + 32 + 64 = 233)$$

$$\therefore \text{Wt. of sulphur present} = \frac{0.774 \times 32}{233} \text{ gm.}$$

\therefore %age of sulphur in the substance

$$= \frac{0.774 \times 32}{233} \times \frac{100}{1.1564} = 6.74$$

(iv) Percentage of oxygen (by difference)

$$\begin{aligned} &= 100 - (65.82 + 5.45 + 6.74) \\ &= 100 - 78.01 = 21.99. \end{aligned}$$

$$C = 65.82\%$$

$$H = 5.45\%$$

$$S = 6.74\%$$

$$O = 21.99\%$$

Exercises

1. 0.6 gm. of an organic substance containing carbon, hydrogen and nitrogen only gave on combustion 1.17 gms. CO_2 and 0.84 gm. H_2O . Calculate the percentage composition of the substance.

2. 0.2 gm. of an organic substance containing C_3H and O gave on combustion 0.04 gm. water and 0.195 gm. CO_2 . Calculate its % age composition.

3. On combustion 0.45 gm of an organic substance gave 0.44 gm. CO_2 and 0.09 gm. H_2O . Find its percentage composition.

4. 0.4092 gm. of an organic substance gave 60.8 m.ls. of moist nitrogen measured $15^\circ C$ and 732.7 mm. pressure. Calculate the percentage of nitrogen in the substance.

5. 0.1877 gm. of an organic compound gave on combustion 31.7 m.ls. of moist nitrogen measured at $14^\circ C$ and 758 mm. pressure. Calculate the percentage of nitrogen in the compound.

6. 0.4422 gm. of an organic substance was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 m.ls. of NH_4SO_4 . The residual acid

required 65.5 m.l.s. of $\frac{N}{2}$ alkali. Find the percentage of nitrogen in the compound.

(P. U. 1944)

7. 0.2398 gm. of an organic substance containing C, H, O gave on combustion 0.3506 gm. of CO_2 and 0.1446 gm. of H_2O . Calculate the percentage composition of the substance.

8. An organic compound gave the following results on analysis :-

0.1335 gm. gave 0.2948 gm. CO_2 and 0.0603 gm. H_2O .
0.085 gm. gave 26.4 m.l.s. of dry nitrogen measured at $27^\circ C$ and 750 mm. pressure. Calculate the percentage of C, H, N in the compound.

9. An organic compound gave the following results :-

0.197 gm. gave 0.293 gm. CO_2 and 0.150 gm. H_2O . By Kjeldahl's method 0.59 gm. required 10 m.l.s. of N. H_2SO_4 for the neutralization of Ammonia. Calculate the percentage composition.

10. 0.301 gm. of an organic substance gave 0.282 gm. of AgBr. Calculate the percentage of Bromine.

11. 0.2865 gm. of an organic substance gave 0.3655 gm. of AgCl. Calculate the percentage of chlorine in the substance.

12. 0.36 gm. of an organic substance gave 0.35 gm. of $BaSO_4$. Find the percentage of sulphur in the substance.

13. 1.395 gm. of an organic substance containing phosphorus, when treated according to Carius' method gave 0.666 gm. of $Mg_2P_2O_7$. Calculate the percentage of phosphorus.

14. 0.369 gm. of a substance gave 0.568 gm. of

AgBr. Calculate the percentage of bromine in the substance.

15. 0.150 gm. of a substance gave 0.075 gm. of AgCl. Calculate the percentage of chlorine.

16. 0.2014 gm. of the substance gave 0.2110 gm of BaSO_4 . Calculate the percentage of sulphur.

17. 0.215 gm. of a substance gave 0.195 gm. of AgI. Calculate the percentage of Iodine in the compound.

18. Calculate the percentage of nitrogen estimated by Kjeldahl's method from the following data:—

1.525 gm. of the substance was decomposed and distilled with NaOH and ammonia collected in 30 m.l.s. of N. HCl. The acid then required 120 m.l.s. of $\frac{\text{N}}{10}$ NaOH solution for neutralisation. (P. U. 1938)

19. 1.15 gms. of the substance was Kjeldahlised and the ammonia produced was collected in 30 m.l.s. of normal solution of HCl. The excess of the acid was then titrated against normal NaOH solution of which 18.4 m. ls. were used for neutralisation. Calculate the amount of nitrogen in the substance (P. U. 1936)

20. 0.1475 gm. of a substance containing nitrogen was distilled into 50 m.l.s. of $\frac{\text{N}}{10}$ HCl and the excess of the acid required 25 m. ls. of $\frac{\text{N}}{10}$ alkali for neutralisation. Calculate the percentage of nitrogen in the substance. (P. U. 1933)

21. 0.246 gm. of an organic substance gave on combustion 0.264 gm. CO_2 and 0.126 gm. H_2O . By the Carius' method 0.369 gm. gave 0.568 gm. of AgBr. Find the percentage composition of the compound. (P. U. 1929)

22. An organic substance containing carbon,

hydrogen, nitrogen and oxygen gave on analysis the following figures:--

0.2001 gm. gave 0.3862 gm. CO_2 and 0.517 gm. H_2O .
0.1061 gm. gave 13.4 m.ls. of dry N_2 at 17°C and 764 mm. Calculate the percentage composition of the substance. (P. U. 1941)

23. 0.2046 gm. of an organic substance gave 30.7 m.ls of moist nitrogen measured at 15°C and 732.7 mm. Calculate the percentage of nitrogen in the substance. (Aq. Tenstion at $15^\circ\text{C}=12.7$ mm. one litre of nitrogen weighs 1.25 gms. at N. T. P). (P. U. 1943)

24. 0.4422 gm. of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 m.ls of $\text{N. H}_2\text{SO}_4$. The residual acid required 65.5 m.ls. of $\frac{\text{N}}{2}$ alkali solution. Find the percentage of nitrogen in the compound. (P. U. 1944)

25. Calculate the percentage of nitrogen estimated by Kjeldahl's method from the following data :—

1.625 gms. of the substance was decomposed and distilled with Caustic Soda and the ammonia collected was passed through 20 m.ls. of normal HCl . The acid then required 20 m.ls. of $\frac{\text{N}}{10}$ NaOH solution for neutralisation.

CHAPTER XIII

EMPIRICAL AND MOLECULAR FORMULA

The composition of an organic compound having been determined, its formula has to be deduced from the results of analysis as follows:—

1. The percentage of each element is divided by its atomic weight to get the relation number of atoms of the various elements present.
2. The quotients thus obtained are then simplified by dividing them by the lowest value. The figures thus obtained represent the simplest ratio of atoms of various elements present.

The formula so obtained which represent the simplest ratio between the atoms of the various elements present in the molecule of a compound, is called Empirical formula.

EXAMPLE 1. *The percentage composition of an organic substance is as follows:*

C=40%, H=6.66%, O=53.34%. Calculate the Empirical formula.

The percentages are as follows:—

$$C=40.00$$

$$H=6.66$$

$$O=53.34$$

Dividing the percentages by atomic weights, we get the relative number of atoms of different elements thus:—

$$C = \frac{40}{12} = 3.33$$

$$H = \frac{6.66}{1} = 6.66$$

$$O = \frac{53.34}{16} = 3.33$$

These numbers are in the ratio 1 : 2 : 1

\therefore the Empirical formula is CH_2O

EXAMPLE 2. *The percentage composition of a substance is C=19.9, H=6.9, N=46.9, O=26.3. Calculate the Empirical formula.*

Dividing the percentages by the respective atomic weights, we have:—

$$C = \frac{19.9}{12} = 1.66$$

$$H = \frac{6.9}{1} = 6.9$$

$$N = \frac{46.9}{14} = 3.35$$

$$O = \frac{26.3}{16} = 1.65.$$

These numbers are in the ratio 1 : 4 : 2 : 1. So that the Empirical formula is $\text{CH}_4\text{N}_2\text{O}$.

EXAMPLE 3. *0.200 gm. of a compound containing carbon, hydrogen, nitrogen and oxygen, gave on combustion 74.6 m.l.s. of nitrogn at N.T.P. In a second experiment, 0.200 gm. yielded 0.147 gm. CO_2 and 0.12 gm. water find its Empirical formula.*

[P.U.1941].

$$\text{Amount of carbon in } 0.147 \text{ gm. } \text{CO}_2 = 0.147 \times \frac{12}{44}$$

$$\text{Percentage of carbon} = 0.147 \times \frac{12}{44} \times \frac{100}{0.2} = 20.4\%$$

$$\text{Amount of hydrogen in } \cdot 12 \text{ gm. of water} = \frac{\cdot 12 \times 2}{18}$$

$$\text{Percentage of hydrogen} = \frac{\cdot 12 \times 2}{18} \times \frac{100}{\cdot 2} = 6\cdot 66\%$$

22400 m.ls. of N_2 weigh 28 gms.

$$\therefore 74\cdot 6 \text{ m.ls. } \text{ } \text{ } = \frac{28 \times 74\cdot 6}{22400}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 74\cdot 6}{22400} \times \frac{100}{\cdot 2}$$

$$= 46\cdot 63\%$$

Percentage of oxygen (by difference)

$$= 100 - (6\cdot 66 + 20\cdot 4 + 46\cdot 63)$$

$$= 100 - 73\cdot 33 = 26\cdot 67\%$$

Percentage of carbon = 20\cdot 4\%

“ “ Hydrogen = 6\cdot 66\%

“ “ Nitrogen = 46\cdot 63\%

“ “ Oxygen = 26\cdot 67\%

Dividing the percentages by respective atomic weights, relative number of atoms of various elements are as follows:—

$$\text{Carbon} = \frac{20\cdot 4}{12} = 1\cdot 67$$

$$\text{Hydrogen} = \frac{6\cdot 66}{1} = 6\cdot 66$$

$$\text{Nitrogen} = \frac{46\cdot 63}{14} = 3\cdot 33$$

$$\text{Oxygen} = \frac{26\cdot 67}{16} = 1\cdot 66$$

Dividing by lowest quotient 1\cdot 66

$$C = \frac{1.67}{1.66} = 1$$

$$H = \frac{6.66}{1.66} = 4$$

$$N = \frac{3.33}{1.66} = 2$$

$$O = \frac{1.66}{1.66} = 1$$

Hence Empirical formula = $\text{CH}_4\text{N}_2\text{O}$

EXAMPLE 4 Calculate the Empirical formula of an organic compound from the following data :—

0.1877 gm. of the compound generated 31.7 m. ls. of moist nitrogen measured at 14°C and 758 mm. pressure.

0.2033 gm. gave on combustion 0.3780 gm. CO_2 and 0.1288 gm. of water.

(Aq. Tension at $14^\circ\text{C} = 12$ mm.)

(P. U. 1939)

$$P = 758 - 12 = 746$$

$$V = 31.7$$

$$T = 273 + 14 = 287$$

$$P_1 = 760$$

$$V_1 = ?$$

$$T_1 = 273$$

$$\frac{PV}{T} = \frac{P_1V_1}{T_1} \quad \therefore V_1 = \frac{PV}{T} \times \frac{T_1}{P_1}$$

$$V_1 = \frac{746 \times 31.7}{287} \times \frac{273}{760} = 29.6$$

Wt. of 22400 m. ls. of nitrogen = 28 gms.

$$\text{.. .. 29.6} = \frac{28 \times 29.6}{22400}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 29.6}{22400} \times \frac{100}{.1877} \\ = 19.72$$

$$\text{Amount of carbon in } .378 \text{ gm. CO}_2 = \frac{.378 \times 12}{44}$$

$$\text{Percentage of carbon} = \frac{.378 \times 12}{44} \times \frac{100}{.2033} \\ = 50.71$$

$$\text{Amount of hydrogen in } .1288 \text{ gm. H}_2\text{O} = \frac{.1288 \times 2}{18}$$

$$\text{Percentage of hydrogen} = \frac{.1288 \times 2}{18} \times \frac{100}{.2033} \\ = 7.039$$

$$\text{Percentage of Nitrogen} = 19.72$$

$$,, \quad ,, \quad \text{Carbon} = 50.71$$

$$,, \quad ,, \quad \text{Hydrogen} = 7.039$$

$$,, \quad ,, \quad \text{Oxygen} = 100 - (19.72 + 50.71 + 7.039) \\ = 100 - 77.47 \\ = 22.53$$

Dividing the percentages by respective atomic weight we have :—

$$\text{C} = \frac{50.71}{12} = 4.226$$

$$\text{H} = \frac{7.039}{1} = 7.039$$

$$\text{N} = \frac{19.72}{14} = 1.409$$

$$\text{O} = \frac{22.53}{16} = 1.408$$

Dividing by lowest quotient :

$$C = \frac{4.226}{1.408} = 3$$

$$H = \frac{7.039}{1.408} = 5$$

$$N = \frac{1.409}{1.408} = 1$$

$$O = \frac{1.408}{1.408} = 1$$

\therefore Empirical formula = C_3H_5NO .

EXAMPLE 5. An organic substance containing C, H, O, and N gave the following results:—

0.21 gm. gave 0.462 gm. CO_2 and 0.1215 gm. water
0.104 gm. of it when distilled with Caustic Soda evolved
ammonia which neutralized 15 m.l.s. of $\frac{N}{20} H_2SO_4$. Calculate
the Empirical formula

(U. P. Board Inter 1948)

Amount of carbon in 0.462 gm. of CO_2

$$= \frac{0.462 \times 12}{44}$$

$$\text{Percentage of carbon} = \frac{0.462 \times 12}{44} \times \frac{100}{0.21}$$

$$= 59.99\%$$

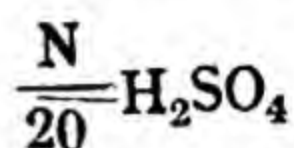
Amount of hydrogen in 0.1215 gm. water

$$= \frac{0.1215 \times 2}{18}$$

$$\text{Percentage of hydrogen} = \frac{0.1215 \times 2}{18} \times \frac{100}{0.21}$$

$$= 6.43\%$$

The ammonia evolved is equivalent to 15 m.l.s. of



$$\text{Nitrogen in 15 m.l.s. of } \frac{\text{N}}{20} \text{ ammonia} = \frac{14}{20} \times \frac{15}{1000}$$

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{14}{20} \times \frac{15}{1000} \times \frac{100}{1.04} \\ &= 10.09 \% \end{aligned}$$

$$\text{Percentage of Carbon} = 59.99$$

$$\text{,, ,, Hydrogen} = 6.43$$

$$\text{,, ,, Nitrogen} = 10.09$$

$$\begin{aligned} \text{,, ,, Oxygen} &= 100 - (59.99 + 6.43 + 10.09) \\ &= 100 - 76.51 \\ &= 23.49 \% \end{aligned}$$

Dividing the percentage by atomic weight we have

$$\text{C} = \frac{59.99}{12} = 4.99$$

$$\text{H} = \frac{6.43}{1} = 6.43$$

$$\text{N} = \frac{10.09}{14} = .72$$

$$\text{O} = \frac{23.49}{16} = 1.46$$

Dividing by lowest quotients we have :

$$\text{C} = \frac{4.99}{.72} = 7$$

$$\text{H} = \frac{6.43}{.72} = 9$$

$$N = \frac{.72}{.72} = 1$$

$$O = \frac{1.46}{.72} = 2$$

\therefore Empirical formula = $C_7H_9NO_2$

EXAMPLE 6. *The analysis of a substance containing carbon, hydrogen, and oxygen gave the following results :—*

$C = 68.84\%$, $H = 4.92\%$ and

(by difference) $O = 26.24\%$. Calculate the Emp. formula.

Dividing the percentage of each element by its atomic weight we get the atomic ratio :

$$C = \frac{68.84}{12} = 5.74$$

$$H = \frac{4.92}{1} = 4.92$$

$$O = \frac{26.24}{16} = 1.64$$

Dividing by the smallest number 1.64, we get the simplest atomic ratio: $C = 3.5$, $H = 3$, $O = 1$.

Hence the Empirical formula of the substance is $C_7H_9O_2$.

Molecular formula. It represents the actual number of atoms of each element present in the molecule of a compound. For its determination:—

Calculate the Empirical formula weight by adding up the atomic weights of various atoms present in the Empirical formula.

Divide the molecular weight by the Empirical formula weight. Let the quotient be x .

Multiply the Empirical formula by x to get the molecular formula.

EXAMPLE. 7. *The Empirical formula of an organic acid is found to be CH_2O . The vapour density of the compound is 30. Find the molecular formula of the acid.*

$$\text{Empirical formula wt.} = 12 + 2 + 16 = 30$$

$$\text{Vapour density} = 30$$

$$\text{Molecular wt.} = 30 \times 2 = 60$$

$$\text{Multiple of Emp. formula} = \frac{60}{30} = 2$$

Molecular formula of the acid is, therefore, $\text{C}_2\text{H}_4\text{O}_2$

EXAMPLE 8. *.228 gm. of an oxy. acid gave .456 gm. CO_2 and .186 gm. H_2O . Find the Molc. formula if its vapour density is 45.1*

$$.456 \text{ gm. } \text{CO}_2 \text{ contain } \frac{.456 \times 12}{44} \text{ gm. carbon}$$

$$\text{Percentage of carbon} = \frac{.456 \times 12}{44} \times \frac{100}{.228} = 54.54\%$$

$$.186 \text{ gm. of water contain } \frac{.186 \times 2}{18} \text{ gm. hydrogen}$$

$$\text{Percentage of hydrogen} = \frac{.186 \times 2}{18} \times \frac{100}{.228} = 9.06\%$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100 - (54.54 + 9.06) \\ &= 100 - 63.6 = 36.4\% \end{aligned}$$

Dividing the percentages by atomic wts., we have:—

$$\text{C} = \frac{54.54}{12} = 4.545$$

$$\text{H} = \frac{9.06}{1} = 9.06$$

$$\text{O} = \frac{36.4}{16} = 2.275$$

Dividing by the lowest quotient

$$C = \frac{4.545}{2.275} = 2$$

$$H = \frac{9.06}{2.275} = 4$$

$$O = \frac{2.275}{2.275} = 1$$

\therefore Empirical formula = C_2H_4O

Empirical formula weight = $12 \times 2 + 4 \times 1 + 16 = 44$

Mole. wt. $\approx 2 \times 45.1 = 90.2$

$$\text{Multiple of Emp. formula} = \frac{90.2}{44} = 2$$

Hence Mole. formula is $(C_2H_4O)_2 = C_4H_8O_2$

EXAMPLE. 9. *A dibasic oxy. acid contained 26.7% carbon, and 2.2% hydrogen. The vapour density of its dimethyl ester was found to be 59. What is the acid?*
(P. U. 1929)

Percentage of C = 26.7

„ „ H = 2.2

„ „ O = $100 - (26.7 + 2.2) = 71.1$

Dividing by At. wt:—

$$C = \frac{26.7}{12} = 2.225$$

$$H = \frac{2.2}{1} = 2.2$$

$$O = \frac{71.1}{16} = 4.44$$

On dividing by lowest quotient the relation No. of

$$C. \text{ atoms} = \frac{2.22}{2.2} = 1$$

On dividing by lowest quotient the relation No, of

$$\text{H atoms} = \frac{2.2}{2.2} = 1$$

$$\text{O} = \frac{4.44}{2.2} = 2$$

\therefore Empirical formula is CHO_2

Empirical formula weight $= 12 + 1 + 32 = 45$

Mole. wt. of dimethyl ester $= 2 \times 59 = 118$

Formula wt. of methyl groups $= 2 \times 15 = 30$

\therefore Mole wt. of acid = Mole wt. of dimethyl ester -
formula wt. of dimethyl + wt. of 2H atoms $= 118 - 30$
 $+ 2 = 90$

\therefore Multiple of Emp. formula $= \frac{90}{45} = 2$

Hence Molecular formula is $\text{C}_2\text{H}_4\text{O}_4$

Since the acid is dibasic, so it is $(\text{COOH})_2$ or oxalic acid

EXAMPLE. 10. 0.2 gm. of an organic monobasic acid gave on combustion 0.505 gm. CO_2 and 0.0892 gm. H_2O . 0.183 gm. of the acid required 15 m.l.s. of $\frac{N}{10}$ NaOH for complete neutralization. Calculate the Molecular weight and the Molecular formula of the acid (P.U. 1945)

$$0.505 \text{ gm. } \text{CO}_2 \text{ contain carbon} = \frac{0.505 \times 12}{44}$$

$$\therefore \text{percentage of carbon} = \frac{0.505 \times 12}{44} \times \frac{100}{0.2} = 68.86 \%$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{0.0892}{0.2} \times 100 = 4.96 \%$$

$$\text{Percentage of oxygen (by difference)} = 100 - (68.86 + 4.96) = 26.18 \%$$

Dividing the percentages by At. wts.

$$C = \frac{68.86}{12} = 5.74$$

$$H = \frac{4.96}{1} = 4.96$$

$$O = \frac{26.18}{16} = 1.64$$

Dividing by lowest quotient

$$C = \frac{5.74}{1.64} = 3.5$$

$$H = \frac{4.96}{1.64} = 3$$

$$O = \frac{1.64}{1.64} = 1$$

Simplest whole number ratio is 7 : 6 : 2

∴ Emp. formula is $C_7H_6O_2$

Emp. formula weight = $84 + 6 + 32 = 122$

The mole. wt. can be found from neutralisation data thus :

15 m.l.s. $\frac{N}{10}$ NaOH neutralize 0.183 gm. acid

1000 m.l.s. N. NaOH .. $\frac{0.183 \times 10 \times 1000}{15}$ gm. acid
= 122 gms. acid

∴ E. wt. of the acid = 122

Mole. wt. = Eq. wt \times Basicity = $122 \times 1 = 122$

Since the Emp. formula weight and the molecular weight are the same, the molecular formula of the acid is also $C_7H_6O_2$.

EXAMPLE. 11. A monobasic acid gave on analysis, the undermentioned data. Calculate the Empirical formula

of the acid and suggest its structured formula. 0.201 gm. gave 0.308 gm. CO_2 and 0.045 gm. H_2O .

0.3 gm. gave 0.282 gm. AgBr . 0.402 gm. were neutralised by 20 m.l.s. of $\frac{N}{10}$ alkali

($\text{Ag}=108$, $\text{Br}=80$)

(P. U. 1941)

$$\text{Percentage of Carbon} = \frac{.308 \times 12}{44} \times \frac{100}{.201} = 41.8\%$$

$$\text{Percentage of Hydrogen} = \frac{.045 \times 2}{18} \times \frac{100}{.201} = 2.4\%$$

$$\text{Percentage of Bromine} = \frac{.282 \times 80}{188} \times \frac{100}{.3} = 40\%$$

$$\text{Percentage of oxygen (by difference)} = 100 - (41.8 + 2.4 + 40) = 15.8\%$$

Dividing the percentage by At. wt. we have atomic ratio as :

$$\text{C} = \frac{41.8}{12} = 3.48$$

$$\text{H} = \frac{2.4}{1} = 2.4$$

$$\text{Br} = \frac{40}{80} = .5$$

$$\text{O} = \frac{15.8}{16} = .99$$

Dividing by lowest quotient

$$\text{C} = \frac{3.48}{.5} = 7$$

$$H = \frac{2.4}{.5} = 5$$

$$Br = \frac{.5}{.5} = 1$$

$$O = \frac{.99}{.5} = 2$$

∴ Empirical formula of the acid is $C_7H_5BrO_2$

Mole. wt. of the acid can be calculated as follows:—

20 m.l.s. of $\frac{N}{10}$ alkali neutralise .402 gm.

$$\therefore 1000 \text{ ,, ,, ,, ,, } \frac{.402 \times 1000}{20}$$

$$\text{and 1000 m.l.s. of N ,, ,, } \frac{.402 \times 1000}{20} \times 10 = 201$$

∴ Equivalent weight of the acid is 201.

$$\begin{aligned} \text{Mole. wt.} &= \text{Eq. wt} \times \text{Basicity} \\ &= 201 \times 1 = 201 \end{aligned}$$

$$\begin{aligned} \therefore \text{Empirical formula weight} &= C_7H_5BrO_2 \\ &= 84 + 5 + 80 + 32 \\ &= 201 \end{aligned}$$

Since the Emp. formula weight and the molecular weight of the acid, are the same, the molecular formula of the acid is also $C_7H_5BrO_2$. And as the acid is mono-basic, its structural formula is $C_6H_4Br \cdot COOH$,

Exercises

1. An organic compound containing carbon, hydrogen, nitrogen and oxygen was found on analysis to yield $C=65\%$, $H=3.5\%$, $N=9.6\%$. Its density is 73.5 as

compared with hydrogen. What is the molecular formula of the compound?

2. 0.5 gm. of an organic compound containing C, H, and O, gave on combustion 0.3 gm. of water and 0.733 gm. of CO_2 . The vapour density compared to hydrogen is 30. What was the Molecular formula of the compound?

(P. U. 1918)

3. .304 gm. CO_2 and .124 gm. water are formed by the combustion of .152 gm. of a substance when V. D. is 45.3. Calculate the molecular formula of the compound.

4. Calculate the formula of the compound whose percentage composition is as follows :

$$\text{C}=52.2, \text{H}=13, \text{O}=34.8$$

5. An organic compound was found to contain 66.6% carbon and 7.4% hydrogen. 0.135 gm. of the same on analysis gave 27.9 m ls. of N_2 at N. T. P. If the Mole. Wt. is 108 calculate the formula of the compound.

(U. P. Inter 1928)

6. 0.246 gm. of an organic substance gave .264 gm. CO_2 and .126 gm. H_2O and .369 gm. of the same substance gave .568 gm. AgBr. What is the Empirical formula of the compound?

(P. U. 1929)

7. .465 gm. of an organic substance gave on combustion 1.32 gms. CO_2 and 315 gm. H_2O . 1.2325 gms. of the same gave 27.8 m.ls. N_2 at N.T.P. Calculate the formula of the substance.

8. 0.2869 gm. of an organic compound gave on combustion 0.6507 gm. CO_2 and 0.2678 gm. H_2O . In a Victor Meyer determination 0.1187 gm. of the compound displaced 47 m.ls. of moist air at 15°C and 772 mm. Deduce the Empirical and Molecular formula. (Aq. Tension at $15^\circ\text{C}=12.7$ mm.)

9. An organic monobasic acid gave the following combustion data:—

0.10 gm. gave 0.2525 gm. CO_2 and 0.0432 gm. water.

0.122 gm. of the acid required 10 m.l.s. of $\frac{\text{N}}{10}$ NaOH for complete neutralisation. What is the acid?

(P. U. 1931)

10. 0.3696 gm. of a compound containing C, H and O, gave on combustion 0.542 gm. CO_2 and 0.2168 gm. H_2O . What is the formula of the substance?

(P. U. Board Inter 1922)

11. An organic compound containing C, H, N and O gave the following result:—

0.205 gm. gave 0.528 gm. CO_2 and 0.0675 gm. water.

1.029 gms. when distilled with caustic soda yielded ammonia which required 14 m.l.s. of $\frac{\text{N}}{2}$. H_2SO_4 for neutralisation. Calculate the formula of the substance.

(U. P. Board 1942)

12. 0.369 gm. of a substance gave on combustion 0.396 gm. CO_2 and 0.189 gm. H_2O . Also 0.246 gm. of the substance gave 0.319 gm. AgBr. What is the formula of the substance?

(P. U. Supp. 1945)

13. An organic substance containing C, H and N gave the following results on analysis:—

0.465 gm. of the substance yielded on combustion 1.32 gm. CO_2 and 0.315 gm. H_2O .

0.2325 gm. of the substance yielded 27.3 m.l.s. of N_2 at N. T. P. Calculate the formula of the substance.

(U. P. Board Inter 1934)

14. 0.6 gm. of an organic substance containing C, H, and N only, gave on complete combustion 1.17 gms. of CO_2 and 0.84 gm. H_2O . With HNO_2 nitrogen was evolved. Identify the substance, if its molecular weight is 45.

(P. U. 1942)

15. An organic substance containing C, H and N was found to give the following results on analysis: 0.20 gm. of the substance gave 0.482 gm. CO_2 , 0.231 gm. H_2O , and 30.8 m.l.s. of N_2 at N. T. P. Calculate the Empirical and the Molecular formulae. (V.D = 36.5 and one litre of N_2 weighs 1.257 gms. at N. T. P.)

(P. U. 1934)

16. An organic substance containing C, H, O, and N gave on analysis the following results:—

0.139 gm. of the substance yielded 0.308 gm. CO_2 and 0.081 gm. water. 0.2085 gm. of the substance when distilled with NaOH , yielded ammonia which required 15 m.l.s. of decinormal solution of sulphuric acid for neutralisation. Calculate the formula of the substance.

(U. P. Board Inter 1940)

17. An organic substance containing C, H, N and O gave on analysis the following results:—

0.425 gm. of the substance yielded 0.484 gm. CO_2 and 0.4365 gm. H_2O .

0.693 gm. of the substance when distilled with NaOH , yielded ammonia which required 18 m.l.s. of seminormal solution of H_2SO_4 for neutralisation. Calculate the formula of the substance.

(U. P. Board Inter 1939)

18. A substance gave the following analytical result:—

C = 54.4, H = 9.09, O = difference.

A vapour density determination by Victor Meyer's method gave the following result:—

0.1 gm. of the substance displaced 27 m.ls. of air measured at 15°C and 745 mm. pressure. Determine the molecular formula (Aq. Tension $15^{\circ}\text{C}=12.7$ mm.)

(P. U. 1937)

19. 0.20 gm. of a compound containing C, H, N and oxygen gave on combustion 74.6 m.ls. of N_2 at N. T. P. In a second experiment 0.20 gm. yielded 0.147 gm. CO_2 and 0.12 gm. water. Find its simplest formula.

(P. U. 1941)

20. Find the formula of an organic compound containing C, H, O and sulphur from the following data:—

0.1668 gm. of the substance on combustion gave 0.454 gm. of CO_2 and 0.0663 gm. H_2O .

0.1254 gm. of the substance on being heated with BaCl_2 and HNO_3 gave 0.1292 gm. BaSO_4 .

[U. P. Board Inter 1943]

21. Calculate the Empirical formula of an organic compound from the following data:—

0.1877 gm. of the compound generated 31.7 m.ls. of moist nitrogen measured at 14°C and 758 mm. pressure. 0.2033 gm. gave on combustion 0.378 gm. CO_2 and 0.1288 gm. water.

[Aq. Tension at $14^{\circ}\text{C}=12$ mm.]

[P. U. 1939]

22. An organic acid containing only C, H, and O, gave the following results on analysis:—

0.324 gm. gave 0.3168 gm. CO_2 and 0.0648 gm. H_2O . The vapour density of its ethyl ester is found to be about 71. What is the constitutional formula of the acid.

23. An organic monobasic acid gave the following results on analysis:—

0.201 gm. gave 0.308 gm. CO_2 and 0.045 gm. H_2O .

0.301 gm. gave 0.282 gm. AgBr. 0.402 gm. were neutralised by 20 m.l.s. $\frac{\text{N}}{10}$ alkali,

Calculate the Empirical formula of the acid and suggest its structural formula.

CHAPTER XIV

DETERMINATION OF MOLECULAR WEIGHTS

[A] **Molecular weight of Volatile substances.** This is determined by Victor Meyer's Method as explained in Part I Chapter VI.

EXAMPLE 1. *In a Victor Meyer apparatus, 0.146 gm. of chloroform displaced 30.5 m.ls. of air, measured over water at 22°C, the barometric pressure being 755 mm. Calculate the molecular weight of chloroform. [Aq. Tension at 22°C = 20 mm.]*

$$P_1 = 755 - 20 = 735 \text{ mm.}$$

$$V_1 = 30.5 \text{ m.ls.}$$

$$T_1 = 273 + 22 = 295^\circ \text{A}$$

$$P_2 = 760 \text{ mm.}$$

$$V_2 = ?$$

$$T_2 = 273^\circ \text{A.}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \therefore V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$V_2 = \frac{30.5 \times 273 \times 735}{295 \times 760} = 27.2 \text{ m.ls.}$$

Hence 0.146 gm. of chloroform when in the state, of vapour would occupy 27.2 m.ls. at N.T.P. Therefore, the weight of the substance that would occupy 22.4

$$\text{litres at N.T.P.} = \frac{0.146 \times 22.4 \times 1000}{27.2} \text{ gm.}$$

$$= 120 \text{ gms.}$$

$$\text{Mole. wt. of chloroform} = 120$$

[B] **Molecular weights of organic acid and bases.**
For the determination of the molecular weights of organic acid and bases, following methods are available :-

[I] **Volumetric method for acids as well as bases.**

It consists in dissolving a known weight of the acid or the base in water and making the solution to a definite volume. It is titrated respectively against a standard alkali or an acid and from the data so obtained the equivalent weight is calculated.

Then Mole. wt. of acid = Eq. wt. \times Basicity

and Mole. wt. of base = Eq. wt. \times Acidity

EXAMPLE 2. 0.272 gm. of an organic monobasic acid required 20 m.l.s. of $\frac{N}{10}$ NaOH for complete neutralisation.

Calculate the molecular weight of the acid.

20 m.l.s. of $\frac{N}{10}$ NaOH = 0.272 gm. acid. But one gm. equivalent of the NaOH must neutralize one gm. equivalent of the acid.

Now one gm. equivalent of NaOH is present in 1000 m.l.s. of N. NaOH solution.

20 m.l.s. of $\frac{N}{10}$ NaOH = 0.272 gm. acid

$$\therefore 1000 \text{ m.l.s. of N. NaOH} = \frac{0.272 \times 1000}{20} \times 10 = 136 \text{ gms.}$$

\therefore Equivalent wt. of the acid is 136

$$\begin{aligned} \text{Mole. wt.} &= \text{Eq. wt.} \times \text{Basicity} \\ &= 136 \times 1 = 136. \end{aligned}$$

EXAMPLE 3. 0.122 gm. of an organic diacid base required 10 m.l.s. of $\frac{N}{10}$ acid for complete neutralization. Calculate the molecular weight of the base.

$$\begin{array}{rcl}
 10 \text{ m.l.s. of } \frac{N}{10} \text{ acid neutralize } 0.122 \text{ gm. of base.} \\
 1000 \text{ ,, ,, } N \text{ ,, ,, } & \frac{0.122 \times 1000}{10} \times 10 & \\
 & = 122 \text{ gms. of base.} &
 \end{array}$$

$$\therefore \text{Eq. Wt. of base} = 122$$

$$\begin{aligned}
 \text{Mole. Wt.} &= \text{Eq. Wt.} \times \text{acidity} \\
 &= 122 \times 2 = 244.
 \end{aligned}$$

II. Silver Salt Method for acids.

The method of finding equivalent weight of organic acids is based upon the fact that they form insoluble silver salts, which on complete ignition leave behind only the metal silver.

A strong solution of silver nitrate is added to a solution of sodium salt of organic acid to precipitate its silver salt. The ppt. is filtered, washed and dried at low temperature. x grams of silver salt are weighed in a crucible and heated gently at first and finally to red heat. Repeated heating, cooling and weighing are carried out till a constant weight (y gms.) of the residual metallic silver is obtained.

Then x gms. of the silver salt has given rise to y gms. of silver. Applying the law of equivalent weights, the values are in the ratio of the equivalents of the silver salt of the acid and silver respectively. The equivalent of silver being 108, that of the silver salt will be

$$\frac{108 \times x}{y}$$

From the equivalent weight of the silver salt of the acid the equivalent weight of the acid can be calculated

by subtracting 107 from it, because the silver atom having the atomic weight 108 is to be replaced by a hydrogen atom having the atomic weight 1. Hence the equivalent of the acid will be $\left(\frac{108 \times x}{y} - 107\right)$

The calculations in details are as follows :—

Calc. Weight of the silver salt taken $= x$ gms.
 Weight of the silver left on ignition $= y$ gms.
 Basicity of the acid $= n$.
 Equivalent weight of silver $= 108$.

Since $\frac{\text{Eq. Wt. of silver salt}}{\text{Eq. Wt. of silver}} = \frac{\text{Wt. of silver salt ignited}}{\text{Wt. of silver left on ignition}}$

\therefore Eq. Wt. of silver salt Ag A. $= \frac{x}{y} \times 108$.

\therefore Eq. Wt. of HA. the organic acid $= \frac{108x}{y} - 108 + 1$.

i.e. (Ag A — Ag + H.)

\therefore Molecular Weight of the acid $= n \left(\frac{108x}{y} - 108 + 1 \right)$

EXAMPLE 4. 2.364 gms. of the silver salt of a dibasic organic acid on ignition left a residue of 1.536 gms. silver. What is the Molecular weight of the acid?

Since $\frac{\text{Eq. Wt. of silver salt}}{\text{Eq. Wt. of silver}} = \frac{\text{Wt. of silver salt ignited}}{\text{Wt. of silver residue.}}$

\therefore Eq. Wt. of silver salt $= \frac{2.364}{1.536} \times 108 = 166$.

\therefore Eq. Wt. of the acid $= 166 - 108 + 1 = 59$.

\therefore Mol. Wt. of acid $= 2 \times 59 = 118$.

EXAMPLE 5. 2143 gm. of the silver salt of a monobasic acid gave on ignition, 0.101 gm. of silver. Calculate its molecular weight.

Wt. of the silver salt = 2143 gm.

Wt. of silver = 0.101 gm.

∴ Equivalent of the silver salt = $\frac{2143 \times 108}{0.101} = 229$.

∴ Eq. Wt. of the acid = $229 - 107 = 122$.

Basicity of the acid = 1

∴ M. Wt. of the acid = $122 \times 1 = 122$.

EXAMPLE 6. The silver salt of a monobasic acid contains 54.8 percent of silver. Calculate its molecular weight.

The silver salt contains 54.8% of silver.

∴ Wt. of the silver salt = 100 gms.

and the Wt. of silver obtained = 54.8 gms.

∴ Equivalent Wt. of the silver salt = $\frac{100 \times 108}{54.8} = 197$

and the Eq. Wt. of the acid = $197 - 107 = 90$.

∴ The Molecular Wt. = 90 (basicity = 1).

III Platini Chloride Method for base.

Organic bases are so weak that they cannot be titrated with acids. In finding their molecular weights advantage is taken of the capacity of organic bases to form with chloroplatinic acid H_2PtCl_6 sparingly soluble crystalline salts which on ignition leave a residue of platinum.

In practice platonic chloride is added to the base in an excess of dilute hydrochloric acid to precipitate the salt. If B represents the monoacid base then the formula of the precipitated salt is $B_2H_2PtCl_6$. It is filtered, washed, dried and a known weight x gm. is completely ignited in a crucible to leave behind only

platinum. The weight of the residual Pt. is found to be y grams.

The formula of the chloroplatinate salt is $B_2H_2PtCl_6$ in the case of a mono-acid base and $B_2H_2PtCl_6$ in the case of a diacid base.

$$\begin{aligned}\text{Molecular Weight of it} &= 2B + 2 + 195 + 35.5 \times 6 \\ &= 2B + 197 + 213.0 \\ &= 2B + 410\end{aligned}$$

$$\text{But } \frac{\text{Wt. of chloroplatinate}}{\text{Wt. of platinum}}$$

$$= \frac{\text{Wt. of chloroplatinate ignited}}{\text{Wt. of platinum left on ignition}}$$

$$\text{Or } \frac{2B + 410}{195} = \frac{x}{y}$$

Since x and y are known from the experiment so B can be calculated.

In the case of the **diacid base**, the result will be

$$\frac{B + 410}{195} = \frac{x}{y}$$

EXAMPLE 7. *·982 gm. of the chloroplatinate salt of a mono-acid amine are ignited in a crucible and ·3445 gm. of platinum are left as residue. Find the molecular weight of the amine*

$$\text{Since } \frac{\text{Wt. of chloroplatinate}}{\text{Wt. of platinum}}$$

$$= \frac{\text{Wt. of chloroplatinate ignited}}{\text{Wt. of platinum left.}}$$

$$\text{Or } \frac{2B + 410}{195} = \frac{0.982}{.3445}$$

$$\text{Or } 2 \times .3445 B + 410 \times .3445 = .982 \times 195$$

$$\text{Or } .689 B + 141.2 = 191.5$$

$$\cdot 689 B = 191 \cdot 5 - 141 \cdot 2 = 50 \cdot 3$$

$$\therefore B = \frac{50 \cdot 3}{\cdot 689} = 73.$$

EXAMPLE 8. 0.400 gm. of the platini chloride of a mono-acid organic base left on ignition 0.125 gm. of platinum. What is the molecular weight of the base.

$$\frac{\text{Wt. of platini chloride}}{\text{Wt. of platinum}}$$

$$= \frac{\text{Wt. of platini chloride ignited}}{\text{Wt. of platinum left.}}$$

$$\text{Or } \frac{2B + 410}{195} = \frac{\cdot 400}{\cdot 125}$$

$$\text{Or } 2 \times \cdot 125 B + 410 \times \cdot 125 = \cdot 400 \times 195$$

$$\text{Or } \cdot 25 B = \cdot 400 \times 195 - 410 \times \cdot 125$$

$$= 26 \cdot 75$$

$$\text{Or } B = \frac{26 \cdot 75}{\cdot 25} = 107$$

EXAMPLE 9. 0.236 gm. of an organic dibasic acid gave on combustion 0.352 gm. CO_2 and 0.108 gm. H_2O .

0.5 gm. of its normal silver salt gave on ignition 0.32 gm. of pure silver. What is the formula of the acid.

$$\text{Percentage of carbon} = \frac{\cdot 352}{\cdot 236} \times \frac{12}{44} \times 100$$

$$= 40 \cdot 67\%$$

$$\text{Percentage of hydrogen} = \frac{\cdot 108}{\cdot 236} \times 100 \times \frac{2}{18}$$

$$= 5 \cdot 08\%$$

$$\text{Percentage of oxygen} = 100 - [40 \cdot 67 + 5 \cdot 08]$$

$$= 100 - 45 \cdot 75$$

$$= 54 \cdot 25\%$$

Dividing the percentages by At. wts. we have atomic ratio:

$$C = \frac{40.7}{12} = 3.39$$

$$H = \frac{5.08}{1} = 5.08$$

$$O = \frac{54.25}{16} = 3.39$$

Dividing by the lowest quotient

$$C = \frac{3.39}{3.39} = 1$$

$$H = \frac{5.08}{3.39} = 1.5$$

$$O = \frac{3.39}{3.39} = 1$$

Simplest whole number ratio is **2 : 3 : 2**

∴ Emp. formula is $C_2H_3O_2$

$$\text{Emp. formula wt.} = 24 + 3 + 32 = 59$$

$$\frac{\text{Wt. of silver salt}}{\text{Wt. of silver}} = \frac{\text{Eq. Wt. of silver salt}}{\text{Eq. Wt. of silver}}$$

$$\text{Eq. Wt. of silver salt} = \frac{108 \times .5}{.32} = 168.7$$

$$\text{Eq. Wt. of the acid} = 168.7 - 108 + 1 = 61.7$$

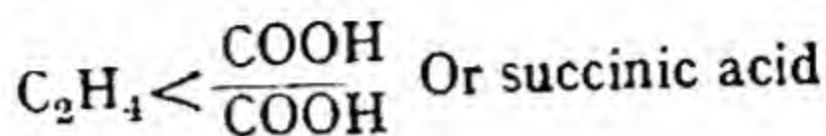
$$\text{Basicity} = 2$$

$$\therefore \text{Mole. Wt.} = 61.7 \times 2 = 123.4$$

$$\text{Multiple of Emp. formula} = \frac{123.4}{59} = 2$$

∴ Molecular formula is $C_4H_6O_4$

As the acid is dibasic, its structural formula will be



EXAMPLE 10. A mono-acid organic base gave the following results on analysis:—

(i) 0.100 gm. gave 0.288 gm. CO_2 and 0.0756 gm. water.

(ii) 0.200 gm. gave 21.8 m.ls. of nitrogen at 15°C and 760 mm. pressure.

(iii) 0.400 gm. of the platinum chloride left on ignition, 0.125 gm. of platinum. What is the molecular formula of the base.

[Punjab B. Sc. 1935]

$$\text{Percentage of carbon} = \frac{0.288 \times 12}{44} \times \frac{100}{0.100} = 78.5\%$$

$$\text{Percentage of hydrogen} = \frac{0.0756 \times 2}{18} \times \frac{100}{0.100} = 8.4\%$$

Vol. of 21.8 m.ls. of nitrogen at N.T.P.

$$= \frac{21.8 \times 273}{288} \\ = 20.66 \text{ m.ls.}$$

Wt. of 20.66 m.ls. of N_2 at N.T.P. = 0.00126×20.66 gm

$$\text{Percentage of nitrogen} = \frac{0.00126 \times 20.66 \times 100}{0.200} \\ = 13.29\%$$

$$\text{Sum of the percentages} = 78.5 + 8.4 + 13.29 \\ = 100.19$$

Therefore there is no oxygen.

Dividing the percentages by At. wts.

$$C = \frac{78.5}{12} = 6.54$$

$$H = \frac{8.4}{1} = 8.4$$

$$N = \frac{13.29}{14} = .95$$

Dividing by lowest quotient.

$$C = \frac{6.54}{.95} = 7$$

$$H = \frac{8.4}{.95} = 9$$

$$N = \frac{.95}{.95} = 1$$

∴ Empirical formula of the base is C_7H_9N .

If B is the formula of the base, the formula of the platini chloride should be $B_2H_2PtCl_6$.

Mole. wt. of platini chloride

$$= 2B + 2 + 195 + 213$$

$$= 2B + 410.$$

Wt. of platinum = 195

A gram molecule of platinic chloride leaves on ignition 195 gms. of platinum. Also .400 gm. of platinic chloride leaves on ignition .125 gm. of platinum.

$$\therefore \frac{2B + 410}{195} = \frac{.400}{.125}$$

$$2 \times .125 B + 410 \times .125 = .400 \times 195$$

$$.25B = .400 \times 195 - 410 \times .125$$

$$= 26.75$$

$$B = \frac{26.75 \times 1}{.25} = 107$$

\therefore Mole. wt. of the base = 107.

Empirical formula wt. = $84 + 9 + 14$
= 107

This is identical with Mole. wt.

Hence the Mole. formula of the base is same as its Empirical formula, i. e. C_7H_9N .

Exercises.

1. In a determination of the molecular weight of a substance by Victor Meyer's method, 0.1680 gm. of the substance gave 49.4 m. ls. of vapour at 20°C and 740 mm. pressure. Calculate the molecular weight of the substance.
(Punjab B.Sc, Agr. 1926)

2. 0.45 gm. of chloroform displaced 91.5 m.ls. of air measured over water at 22°C and 755 mm. pressure. Calculate the vapour density and the molecular weight of the substance (Aq. Tension = 20 mm.)

3. In a Victor Meyer determination 0.18 gm. of a volatile organic substance displaced 37.5 m.ls. of air collected over water at 14°C and 763 mm. pressure.

Find the molecular weight of the substance.

(Aq. Tension at 14°C = 12 mm.)

4. 0.6 gm. of a volatile organic substance displaced 123 m.ls. of moist air at 20°C and 757.4 mm. pressure.

Find the molecular weight.

(P. U. 1920)

5. In a Victor Meyer determination 0.232 gms. of a volatile organic substance displaced 74 m.ls. of moist air at 11°C and 752 mm. pressure. Find the mole. wt. of the substance.

(Aq. Tension at 11°C = 9 mm.)

6. 0.5 gm. of a volatile organic liquid displaced 112 m.l.s. of moist air at 27°C and 760 mm. pressure. Calculate the mole. wt. of the substance.

(Aq. Tension at $27^{\circ}\text{C}=25$ mm.)

7. One gm. of a silver salt of a dibasic organic acid gave on ignition a residue of 0.71 gm. of metallic silver. What is the mole. wt. of the acid?

8. Calculate the molecular wt. of a monobasic organic acid 0.8352 gm. of silver salt of which gave on ignition 0.2939 gm. of silver.

9. 0.2954 gm. of silver salt of a dibasic organic acid was ignited and the silver left behind was 0.192 gm. Calculate the mole. wt. of the acid.

10. 0.435 gm. of silver salt of a dibasic acid on ignition gave 0.31 gm. of silver. Find its mole. wt.

11. 0.345 gm. of silver salt of a monobasic acid gave on ignition 0.191 gm. of metallic silver. What is the mole. wt. of the acid?

12. 0.607 gm. of the silver salt of a tribasic organic acid was completely decomposed by heat and gave a residue of 0.370 gm. of silver. Find the mole. wt. of the acid.

(P. U. 1946)

13. 0.5 gm. of the silver salt of a dibasic organic acid gave on combustion 0.32 gm. of pure silver. What is the molecular wt. of the acid?

14. 0.2214 gm. of the silver salt of a dibasic acid gave 0.144 gm. of silver. Calculate the molecular wt. of the acid.

(P. U. 1937)

15. 0.701 gm. of the chloroplatinate of a monoacid base gave on ignition 0.2302 gm. of platinum. Calculate the molecular weight of the base.

16. 0.9328 gm. of the chloroplatinate of a mono-acid amine were ignited to leave behind Pt. which weighed 0.3445 gm. Determine the molecular wt. of the amine.

17. 0.52 gm. of the platini chloride of a monoacid organic base left 0.1625 gm. of platinum as residue on ignition. Calculate the molecular weight of the base.

18. On combustion 0.324 gm. of an anhydrous dibasic organic acid containing only C, H and O gave 0.3168 gm. CO_2 and 0.0648 gm. H_2O . 0.5 gm. of the silver salt gave on ignition 0.355 gm. of metallic silver. Calculate the Empirical formula of the acid and gave its constitutional formula. (P. U. 1943)

19. An organic compound gave $\text{C}=61.00\%$, $\text{H}=15.21\%$, $\text{N}=23.71\%$. Its vapour density was approx. 30. Give possible structural formula. (Delhi Inter 1939)

20. 0.2 gm. of an anhydrous acid gave on combustion 0.040 gm. H_2O and 0.195 gm. CO_2 . The acid is found to be dibasic and 0.5 gm. of the silver salt leaves 0.355 gm. silver. What is the simplest formula of the substance and what is its molecular formula. What acid can this be? (P. U. Supp. 1944)

21. On combustion 0.45 gm. of a dibasic organic acid gave oxygen CO_2 and 0.49 gm. of water.

0.76 gm. of its silver salt gave 0.54 gm. of silver on ignition. What is the acid? (P. U. 1938)

22. An organic substance (A) containing oxygen gave the following results:—

$\text{C}=79.24\%$, $\text{H}=5.66\%$. Its vapour density = 53.1. On oxidation (A) was converted into a monobasic acid (B) 0.61 gm. of which required 22.5 m.ls. of $\text{N}/4.5 \text{ KOH}$. for complete neutralisation. What were the substances (A and B) (Delhi Inter. 1938)

CHAPTER XV

GAS ANALYSIS

1. The determination of compositions of gases is based on Gay-Lussac's Law and Avogadro's hypothesis.

Gay-Lussac's Law of Volumes:— When two or more gases react they do so in volumes that bear simple ratio to one another as well as to those of the products if gaseous.

For example, when hydrogen and chlorine combine to form hydrochloric acid gas, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas.

Avogadro's Hypothesis may be enunciated as follows:—

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

2. **Composition of gases.** In the determination of the composition of gases, a known volume of the mixture is mixed up with a known volume of oxygen and the mixture is exploded. The volume of the resultant mixture is measured above 100°C . The mixture is then cooled to atmospheric temperature, when the water vapour present in the mixture gets condensed to the liquid form. The consequent decrease in volume therefore, is equal to the volume of water produced during the reaction. The other gases present in the mixture are measured by dissolving them in their respective solvents so that carbon dioxide is absorbed by caustic potash solution, oxygen by alkaline pyrogallol solution and nitrogen is measured by difference.

Knowing in this way, the volume of the gas exploded and those of the products formed, the composition of the gas can be calculated and the molecular formula can also be obtained by the application of Avogadro's hypothesis. The following examples clearly explain the method used in such cases.

EXAMPLE. 1. *20 m.ls of a hydrocarbon were mixed up with 50 m.ls. of oxygen and the mixture exploded. After explosion the volume of the mixture was found to be 70 m.ls. On cooling, there was a contraction of 40 m.ls. and on passing through caustic potash solution, there was a further contraction of 20 m.ls., the remaining 10 m.ls. being found to be pure oxygen. Calculate the formula of the hydrocarbon.*

Volume of hydrocarbon = 20 m.ls.

Volume after explosion = 70 m.ls

Contraction on cooling = 40 m.ls.

„ after absorption
by KOH. = 20 m.ls.

∴ volume of water formed = 40 m.ls.
and volume of carbon

dioxide formed = 20 m.ls.

∴ 20 m.ls. of the hydrocarbon gives 40 m.ls. of water and 20 m.ls. of carbon dioxide.

Or 1 vol. of the hydrocarbon gives 2 vols. of water and 1 vol. of carbon dioxide.

Applying Avogadro's hypothesis we get :

1 molecule of the hydrocarbon gives 2 molecules of water and 1 molecule of carbon dioxide.

Now 1 molecule of carbon dioxide contains 1 atom of carbon and 2 molecules of water contain 4 atoms of hydrogen.

\therefore 1 molecule of the hydrocarbon contains 1 atom of carbon and 4 atoms of hydrogen

Hence the formula is CH_4 .

EXAMPLE. 2. 5 m.l.s. of a hydrocarbon were mixed up with 30 m.l.s. of oxygen and the mixture exploded. The volume after explosion was found to be 40 m.l.s. On cooling it contracted to 20 m.l.s., and on further passing it through KOH solution 5 m.l.s. of the gas were obtained which was found to be oxygen. Calculate the molecular formula of the gas.

Volume of the hydrocarbon used = 5 m.l.s.

Wt. of oxygen added = 30 m.l.s.

Volume after explosion = 40 m.l.s.

Volume after cooling = 20 m.l.s.

Volume after passing through KOH = 5 m.l.s.

\therefore volume of water formed = decrease in volume on cooling = $40 - 20 = 20$ m.l.s.

Volume of CO_2 formed = decrease in volume after absorption with KOH = $20 - 5 = 15$ m.l.s.

\therefore 5 m.l.s. of the hydrocarbon gives 20 m.l.s. of water and 15 m.l.s. of carbon dioxide.

Or 1 vol. of the hydrocarbon gives 4 vols. of water and 3 vols. of carbon dioxide.

Applying Avogadro's hypothesis, we get :

1 molecule of the hydrocarbon gives 4 molecules of water and 3 molecules of carbon dioxide.

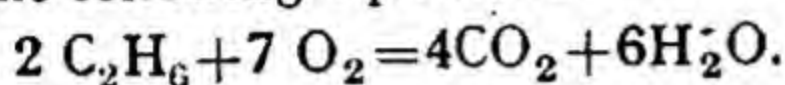
\therefore 1 molecule of the hydrocarbon contains 8 atoms of hydrogen and 3 atoms of carbon.

\therefore the formula of the hydrocarbon is C_3H_8 .

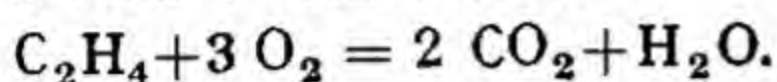
EXAMPLE 3. 60 m.l.s. of a mixture of ethane (C_2H_6) and ethylene (C_2H_4) were exploded with 200 m.l.s. of oxygen. The resulting gas contained 120 m.l.s. of

carbon dioxide and 10 m. ls. of oxygen. Calculate the percentage composition of the original mixture.

Ethane and ethylene explode with oxygen according to the following equations:—



2 vols. 7 vols. 4 vols.



Suppose the volume of ethane = x m.ls.

\therefore the volume of ethylene = $(60 - x)$ m.ls.

Now 2 vols. of ethane require 7 volumes of oxygen.

$\therefore x$ m.ls. $\frac{7x}{2}$ m.ls. ..

and 1 vol. of ethylene requires 3 vols. of oxygen.

$\therefore (60 - x)$ m.ls. 3 $(60 - x)$ m.ls. oxygen

Now the total vol. of oxygen used = 190 m.ls.

$$\therefore \frac{7x}{2} + 3(60 - x) = 190.$$

$$\text{or } 7x + 360 - 6x = 380.$$

$$x = 20$$

\therefore volume of ethane = 20 m.ls.

and the volume of ethylene = $60 - 20 = 40$ m.ls.

EXAMPLE 4. A sample of coal gas contains 45% hydrogen, 30% methane (CH_4), 20% carbon monoxide and 5% acetylene (C_2H_2). 100 vols. of it were mixed up with 160 vols. of oxygen and exploded. Calculate the volume and composition of the resulting mixture (all being dry gases).

100 vols. of the coal gas will contain

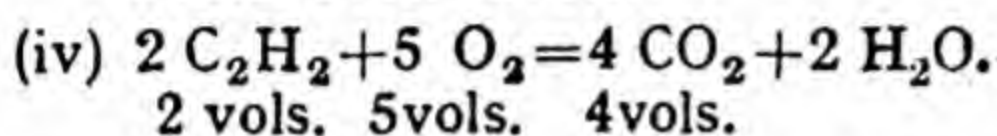
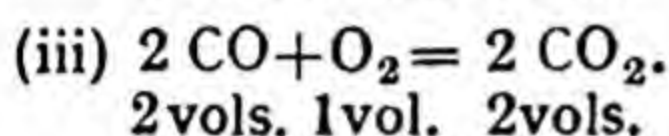
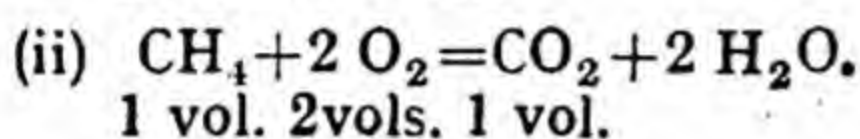
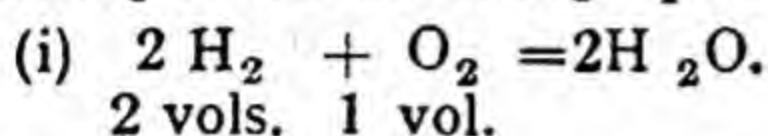
45 vols. of hydrogen

30 vols. of methane

20 vols. of carbon monoxide

and 5 vols. of acetylene.

On explosion, the gases will combine with oxygen according to the following equations:—



The amounts of water will not count as the gases are to be measured dry.

	Volumes of Oxygen used up by the gases	Vols. of carbon dioxide produced.
[a] Hydrogen	$45 \times \frac{1}{2} = 22.5$ vols.	nil
[b] Methane	$30 \times 2 = 60$ vols.	30 vols.
[c] Carbon monoxide	$20 \times \frac{1}{2} = 10$ vols.	20 vols.
[d] Acetylene	$5 \times \frac{5}{2} = \frac{25}{2} = 12.5$ vols.	$5 \times \frac{4}{2} = 10$ vols.
Total	... 105 vols.	60 vols.

\therefore the total volume of oxygen used = 105 vols.

and the total vol. of carbon dioxide = 60 vols.
 \therefore left = $160 - 105 = 55$ vols.

Total volume of the mixture = $60 + 55 = 115$ vols.

Containing 55 vols. of oxygen and 60 vols. of carbon dioxide.

EXAMPLE 5. 50 m.ls. of a mixture of hydrogen, marsh gas and nitrogen were exploded with 400 m.ls. of air. The volume of the gases after explosion and

cooling was 375 m.ls. and after absorption with KOH 375 m.ls. of the mixture were left. Calculate the percentage composition of the original mixture.

Vol. of the mixture used = 50 m.ls.

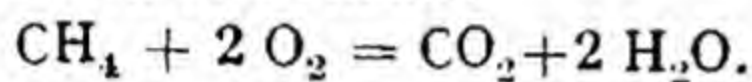
Vol. of air added = 400 m.ls.

Vol. after explosion and cooling = 375 m.ls.

Vol. after absorption with KOH = 345 m.ls.

[1] The volume of carbon dioxide produced
= the contraction of volume on absorption with KOH
= $375 - 345 = 30$ m.ls.

∴ 30 m.ls. of carbon dioxide were obtained on combustion of methane.



1 vol. 2 vols. 1 vol.

Now 1 vol. of methane gives 1 vol. of carbon dioxide.

∴ 30 m.ls. of CO_2 were obtained from 30 m.ls. of methane.

∴ the volume of methane in the mixture = 30 m.ls.

∴ vol. of nitrogen and hydrogen = $50 - 30 = 20$ m.ls.

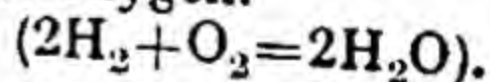
[2] The total vol. of air added = 400 m.ls.

∴ " " " oxygen " = $400 \times \frac{1}{5} = 80$ m.ls.

Now suppose the vol. of hydrogen in the mixture = x m.ls.

∴ the vol. of nitrogen in the mixture = $(20 - x)$ m.ls.

2 vols. of hydrogen require 1 vol. of oxygen.



∴ x m.ls. of hydrogen will combine with $\frac{x}{2}$ m.ls.

and 30 m.ls. of methane will combine with 60 m.ls. of oxygen.
of oxygen.

$$\therefore \text{total vol. of oxygen used} = 60 + \frac{x}{2} \text{ m.l.s.}$$

$$\therefore \left. \begin{array}{l} \text{total vol. oxygen left} \\ \text{unused in the final mixture} \end{array} \right\} \begin{array}{l} = 80 - (60 + \frac{x}{2}) \\ = (20 - \frac{x}{2}) \text{ m.l.s.} \end{array}$$

(3) The total volume left after the absorption with KOH = 345 m.l.s.

It contains—

[i] N_2 that was present in the air = $400 - 80 = 320$ m.l.s.

[ii] N_2 that was present in the mixture = $(20 - x)$ m.l.s.

[iii] Oxygen that was left unused = $(20 - \frac{x}{2})$ m.l.s.

$$\therefore 320 + (20 - x) + (20 - \frac{x}{2}) = 345 \text{ m.l.s.}$$

$$360 - \frac{3x}{2} = 345 \text{ m.l.s.}$$

$$\frac{3x}{2} = 360 - 345$$

$$\frac{3x}{2} = 15$$

$$3x = 30$$

$$x = 10$$

\therefore the volume of hydrogen = 10 m.l.s.

and the volume of nitrogen = 10 m.l.s.

\therefore the composition of the mixture is

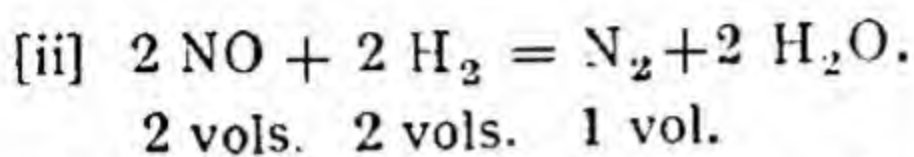
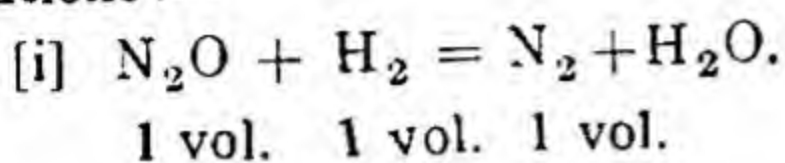
Hydrogen = 10 m.l.s.

methane = 30 m.l.s.

nitrogen = 10 m.l.s.

EXAMPLE 6. 50 m.l.s. of a mixture of nitrous oxide (N_2O) and nitric oxide (NO) were mixed with 100 m.l.s. of hydrogen and the mixture exploded. 40 m.l.s. of nitrogen remained. Find the composition of the mixture.

The reactions may be represented by the following equations:—



Suppose the vol. of $\text{N}_2\text{O} = x$ m.ls.

then the vol. of $\text{NO} = (50 - x)$ m.ls.

Now from (i) 1 vol. nitrous oxide gives 1 vol. of nitrogen

$\therefore x$ m.ls. of nitrous oxide gives x m.ls. of nitrogen.
and from (ii) 2 vols. of nitric oxide gives 1 vol. of nitrogen

$$\therefore (50 - x) \text{ m.ls.} \quad \dots \quad \dots \quad \frac{50 - x}{2} \text{ m.ls of N}_2$$

But the total vol. of nitrogen formed = 40 m.ls.

$$\therefore x + \frac{50 - x}{2} = 40$$

$$\text{Or } 2x + 50 - x = 80.$$

$$\text{Or } x = 30.$$

\therefore volume of nitrous oxide = 30 m.ls.

and „ nitric oxide = $50 - 30 = 20$ m.ls.

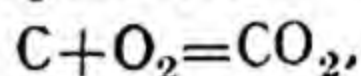
3. Calculation of the formula of a hydrocarbon when the volume of water is not given.

In the problems on the determination of the formula of a hydrocarbon, the volume of the resulting gas after explosion is measured **on cooling**, so that it is not possible to get the volume of water as the volume has been measured after the condensation of the water formed.

Therefore we can directly calculate only the volume of carbon dioxide formed.

In such case the volume of water formed is calculated

indirectly by measuring the amount of oxygen used in the explosion and that used for the oxidation of carbon into carbon dioxide by using the following equation:—



So that 1 vol. of carbon dioxide requires 1 vol. of oxygen. In this way we can calculate the volume of oxygen used for the formation of water by subtraction.

Now the volume of oxygen used for the formation of water being known, the volume of water formed can be directly calculated (2 vols. of water are obtained from 1 vol. of oxygen $2H_2 + O_2 = 2H_2O$).

The formula of the hydrocarbon can then be calculated as explained above.

EXAMPLE 7. 20 m.ls. of a hydrocarbon were mixed with 80m.ls. of oxygen and the mixture exploded.

The volume after explosion and cooling was found to be 60 m.ls. On passing through KOH solution, there was a contraction of 40 m.ls. the remaining 20m.ls. being found to be oxygen. Calculated the formula of the hydrocarbon.

Volume of hydrocarbon = 20 m.ls.

Volume of oxygen added = 80 m.ls.

Volume after cooling = 60 m.ls.

Volume after absorption with KOH = 20 m.ls.

1. The volume of CO_2 = the decrease in volume on absorption with KOH = 40 m.ls.

(2) volume of oxygen used for explosion = $80 - 20$
= 60 m.ls.

and the volume of oxygen used for getting 40 m.ls. of CO_2 ,
= 40 m.ls. ($C + O_2 = CO_2$).

1. vol 1. vol

∴ vol. of oxygen used for producing water

$$= 60 - 40 = 20 \text{ m.l.s.}$$

Now 1 vol. of oxygen is used for getting 2 vols. of water ($2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$)

∴ 20 m.l.s. of oxygen will give 40 m.l.s. of water.

(3) ∴ 20 m.l.s. of hydrocarbon give 40 m.l.s. of CO_2 and 40 m.l.s. of H_2O .

∴ 1 vol of the hydrocarbon gives 2 vols. CO_2 and 2 vols. of H_2O .

Apply Avogadro's hypothesis, we get 1 molecule of hydrocarbon gives 2 molecules of CO_2 and 2 molecules of H_2O .

∴ 1 molecule of the hydrocarbon contains 2 atoms of carbon and 4 atoms hydrogen.

∴ the formula of the hydrocarbon = C_2H_4 .

EXAMPLE 8. 10 m.l.s. of a hydrocarbon were mixed with 50 m.l.s. of oxygen and the mixture exploded. The volume after explosion and cooling was found to be 35 m.l.s. On absorption with caustic potash, 5 m.l.s. of the gas was left which was found to be oxygen. Calculate the formula of the hydrocarbon.

Vol. of the hydrocarbon = 10 m.l.s.

Vol. of oxygen added = 50 m.l.s.

Vol. after cooling = 35 m.l.s.

Vol. after treatment with KOH = 5 m.l.s.

(1) Volume of carbon dioxide = contraction with KOH
 $= 35 - 5 = 30 \text{ m.l.s.}$

(2) Volume of oxygen used in explosion = $50 - 5 = 45 \text{ m.l.s.}$

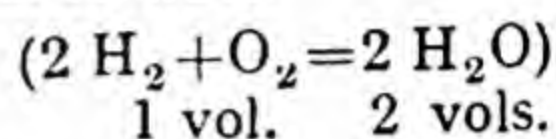
Volume of oxygen used for carbon dioxide

$(\text{C} + \text{O}_2 = \text{CO}_2) = 30 \text{ m.l.s.}$

1 vol. 1 vol

\therefore volume of oxygen used for water $= 45 - 30$
 $= 15$ m.ls,

Now 1 vol. of oxygen gives 2 vols. of water



\therefore 15 m.ls. of oxygen gives 30 m.ls. of water.

(3) \therefore 10 m.ls. of the hydrocarbon gives 30 m.ls. of CO_2 and 30 m.ls. of H_2O .

Or 1 vol. of the hydrocarbon gives 3 vols. of CO_2 and 3 vols. of H_2O .

\therefore 1 molecule of the hydrocarbon gives 3 molecules of CO_2 and 3 molecules of H_2O .

\therefore 1 molecule of the hydrocarbon contains 3 atoms of carbon and 6 atoms of hydrogen.

\therefore the formula of the hydrocarbon $= \text{C}_3\text{H}_6$.

Exercises

1. 20 m.ls. of ethylene were mixed with 80 m.ls. of oxygen and the mixture exploded. Calculate the volume and composition of the mixture of gases.

(i) after explosion, (ii) on cooling, (iii) on absorption with KOH.

2. 15 m.ls. of a mixture of nitrogen and oxygen were mixed with 30 m.ls. of hydrogen. The volume after explosion was found to be 30 m.ls. Calculate the %age composition of the mixture. (All measurements were done at same temperature and pressure.)

3. 15 m.ls. of a hydrocarbon were mixed up with 50 m.ls. of oxygen and the mixture exploded in a eudiometer. After explosion the volume was found to be 65 m.ls. On cooling to the room temperature the volume was reduced to 35 m.ls. On absorption with KOH solution there was a further diminution of volume by 15 m.ls. The residual gas was found to be oxygen. Calculate the molecular formula of the hydrocarbon.

4. 10 m.l.s. of a hydrocarbon mixed up with 60 m.l.s. of oxygen and the mixture exploded. The volume after explosion was found to be 60 m.l.s. which, on cooling, contracted to 40 m.l.s. On absorption with KOH solution there was a further contraction of 20 m.l.s., the remaining 10 m.l.s. being found to be oxygen. Calculate the formula of the hydrocarbon.

5. What volume of atmospheric air at N. T. P. is necessary to burn completely 8 litres of carbon monoxide at 20°C and 740 mm. pressure.

(P. U.)

6. A sample of coal gas contains 50% hydrogen, 30% marsh gas, 14% carbonic oxide and 6% ethylene. 100 m.l.s. of the gas are mixed up with 150 m.l.s. of oxygen and the mixture exploded. What will be the volume and composition of the resulting gas when cooled to the ordinary temperature.

(P. U.)

7. 10 m.l.s. of ethylene were mixed with 45 m.l.s. of oxygen. Calculate the volume of the gases (i) after explosion, (ii) on cooling and (iii) on treatment with KOH.

8. 20 m.l.s. of a hydrocarbon were mixed up with 250 m.l.s. of air. The volume after explosion was found to be 270 m.l.s. On cooling the contraction of 40 m.l.s. took place and on passing through KOH solution, a further contraction of 20 m.l.s. took place and the remaining 210 m.l.s. was found to be a mixture of nitrogen and oxygen. What was the composition of the hydrocarbon and what is the composition of the remaining mixture?

9. 12 m.l.s. of a gaseous hydrocarbon were mixed up with 90 m.l.s. of oxygen and the mixture exploded. After explosion the volume was 72 m.l.s. and on adding KOH 36 m.l.s. of the gas disappeared leaving oxygen only. What is the molecular formula of the hydrocarbon? All the above measurements were made at 15°C and 755 mm.

pressure, the gases being saturated with moisture. (Aq. Tension at $18^{\circ}\text{C}=12.7$ mm.)

10. 20 m.ls. of a hydrocarbon were mixed up with 80 m.ls. of oxygen and the mixture exploded. The volume after explosion and cooling was found to be 70 m.ls. and on passing KOH solution, 30 m.ls. of the gas were left which was found to be oxygen. Calculate the molecular formula of the hydrocarbon.

11. 40 m.ls. of a mixture of hydrogen, methane and nitrogen, was exploded with 10 m.ls. of oxygen. After cooling the residual gas measured 36.5 m.ls. On treatment with KOH, the volume diminished to 33.5 m.ls. and in treatment with alkaline pyrogallor to 32 m.ls. which was found to be nitrogen. Calculate the percentage composition of the mixture.

(P. U. 1928)

12. 40 m.ls. of a mixture of CO and C_2H_2 gases are mixed with excess of oxygen in a eudiometer and exploded. After cooling the volume was noted to be 124 m.ls. and after treatment with KOH the volume was reduced to 68 m.ls. Find the percentage composition of the original mixture.

13. 20 m.ls. of a gaseous hydrocarbon were exploded with 66 m.ls. of oxygen. The residual gases after cooling occupied 56 m.ls. On the treatment with KOH, the volume decreased to 16 m.ls. What is the formula of the hydrocarbon?

(P. U. 1935)

14. 100 m.ls. of a mixture of CO and CH_4 were mixed up with 170 m.ls. of oxygen and exploded. The amount of CO_2 formed was 100 m.ls. and no residue was left. What was the composition of the mixture?

(P. U. 1922)

15. 25 m.ls. of a hydrocarbon were sparked with 85 m.ls. of oxygen. There was no immediate contraction

in volume of 37.5 m.l.s. and on adding NaOH solution a further contraction of 50 m.l.s. occurred. Find the formula of the hydrocarbon. (*P. U. 1940*)

16. 10 m.l.s. of a hydrocarbon mixed with 60 m.l.s. of oxygen were exploded in a eudiometer tube. The explosion was followed by a 25 m.l.s. decrease in volume. On introducing caustic potash into the tube, a further decrease in volume occurred; and the final gas, found by test to be oxygen only, occupied 15 m.l.s. Determine the formula of the hydrocarbon and name it.

(*E. P. Univ. 1948*)

17. 12 m.l.s. of a hydrocarbon were mixed with excess of air and the mixture exploded. After cooling a contraction in volume of 36 m.l.s. occurred. Addition of KOH produced the same contraction in volume. Determine its molecular formula.

18. 15 m.l.s. of a mixture of CO and C_2H_4 required 30 m.l.s. of oxygen for complete combustion. After cooling the residual gases occupied 24 m.l.s. Determine the percentage composition of the mixture.

19. 20 m.l.s. of a gaseous hydrocarbon were mixed up with 80 m.l.s. of oxygen. After explosion and cooling the volume was found to be 70 m.l.s. The addition of caustic potash reduced the volume by 40 m.l.s. and oxygen only was left behind. Calculate the molecular formula of the gas.

20. 15 m.l.s. of a hydrocarbon were mixed with 50 m.l.s. of oxygen and the mixture was exploded. After cooling the volume of the gases was found to be 35 m.l.s. on addition of KOH 20 m.l.s. of the oxygen were left. What was the hydrocarbon?

CHAPTER XVI

MISCELLANEOUS EXAMPLES

1. *The density of oxygen is 16 and that of nitrogen is 14 at N.T.P. At what temperature will oxygen have the same density as nitrogen at 0°C, if the pressure remains constant.*

Density of nitrogen at 0°C = 14

Density of oxygen at 0°C = 16

According to Charles Law, the volume of a gas is directly proportional to the absolute temperatures.

But volumes are inversely proportional to densities.

∴ densities are inversely proportional to absolute temperatures.

Now suppose oxygen has 14 as density at x°C

$$\therefore \frac{273}{273+x} = \frac{14}{16} = \frac{7}{8}$$

$$\text{Or } 2184 = 1911 + 7x.$$

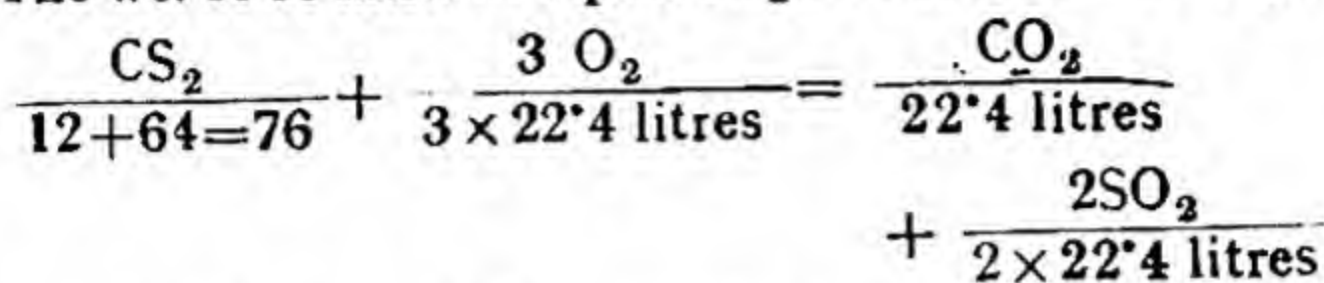
$$\therefore 7x = 2184 - 1911 = 273.$$

$$\therefore x = \frac{273}{7} = 39$$

∴ oxygen has the same density as nitrogen at 0°C at 39°C.

2. *10 m.ls. of liquid carbon disulphide (Sp. gr. 2.63) are burnt in oxygen according to the following equation $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$. Find the volume of oxygen necessary to burn this liquid and the volume of resulting gases measured at N.T.P.*

The wt. of 10 m.l.s. of liquid $\text{CS}_2 = 10 \times 2.63 = 26.3$ gms



So that 76 gms. of CS_2 require 67.2 litres of oxygen.

$$\therefore 26.3 \text{ gms. require } \frac{67.2 \times 26.3}{76} = 23.254 \text{ litres}$$

of oxygen

Similarly 76 gms. of CS_2 produce 22.4 litres of CO_2
and 44.8 litres of SO_2

$$\therefore 26.3 \text{ gms. " " } \frac{22.4 \times 26.3}{76} \text{ litres of}$$

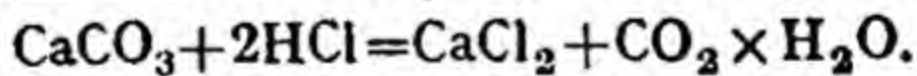
$$\text{CO}_2 \text{ and } \frac{44.8 \times 26.3}{76} \text{ litres of SO}_2$$

$$\therefore \text{vol. of CO}_2 \text{ formed} = \frac{22.4 \times 26.3}{76} = 7.751 \text{ litres}$$

$$\text{and vol. of SO}_2 \text{ formed} = \frac{44.8 \times 26.3}{76} = 15.502 \text{ litres}$$

3. What weight of 20% by wt. of hydrochloric acid solution in water will be required to completely react with 50 gms. of calcium carbonate? What will be the weight and volume of the gas evolved in this reaction?

(a) The reaction will take place according to this equation



100

73

44

22.4 litres.

So that 100 gms. of the carbonate will react with

73 gms. of pure acid.

\therefore 50 gms. of the carbonate will react with 36.5 gms.
of pure acid.

but the acid used is 20% pure.

∴ 36.5 gms. of pure acid will be present in

$$\frac{36.5 \times 100}{20} = 182.5 \text{ gms. of the given acid}$$

(b) The gas formed during the reaction is Carbon Dioxide and 100 gms. of the carbonate produce 44 gms. of the gas.

∴ 50 gms. will produce $\frac{44 \times 50}{100} = 22$ gms. of the gas.

The volume of the gas evolved from 100 gms. of the carbonate = 22.4 litres.

∴ The volume of the gas evolved from 50 gms. of carbonate = 11.2 litres.

4. *One gram of a silver ore was dissolved in nitric acid and the silver present was precipitated with hydrochloric acid. The resulting silver chloride was dried and weighed 0.788 gm. Calculate the percentage of silver in the ore.*

Wt. of the silver ore taken = 1 gm.

Wt. of silver chloride formed = 0.788 gm.

∴ Wt. of silver present = $\frac{0.788 \times 108}{143.5}$ (143.5 gms. of

AgCl contain 108 gms. of silver),
= 0.593 gm.

∴ percentage of silver = $\frac{0.593 \times 100}{1} = 59.3$.

5. *The same current deposits 0.0108 gm. of silver in silver nitrate cell and 0.00315 gm. copper in copper sulphate cell. Calculate the equivalent weight of copper, that of silver being 108.*

The amounts deposited are in the ratio of their equivalent weights.

So that 0.0108 gm. of silver is equivalent to 0.00315 gm. of copper.

\therefore 108 gms. of silver is equivalent to $\frac{0.00315 \times 108}{0.0108}$
 $= 31.5$ gm. of copper

\therefore the Eq. Wt. of copper = 31.5

6. The molecular wt. of a substance is 52.8. Find its density referred to air = 1 (Wt. of one litre of air = 1.293 gm.) and its normal density.

It contains 46.08% carbon and 53.92% nitrogen.

What is the substance?

What volume of nitrogen and carbon dioxide will be formed by exploding 1 litre of it with oxygen?

The molecular wt. of the substance = 52.8

(a) \therefore 22.4 litres of the substance weigh = 52.8 gms.

\therefore 1 litre " " " = $\frac{52.8}{22.4}$
 $= 2.35$ gms.

\therefore the normal density of the substance = 2.35 gm. per litre

(b) The normal density of air = 1.293 gms. per litre.

\therefore density of the substance as compared with air = 1

$$= \frac{2.35}{1.293} = 1.81$$

(c) The percentage composition is :—

C = 46.08. Dividing with At. wts. Ratio of no. of atoms

3.8 1

N = 53.92 3.8 1

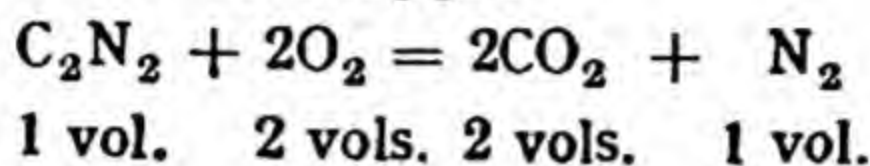
\therefore the Empirical formula = CN.

The Mol. Wt. = 52.8

The Empirical formula Wt. = 12 + 14 = 26.

\therefore the molecular formula = C_2N_2 — which is cyanogen.

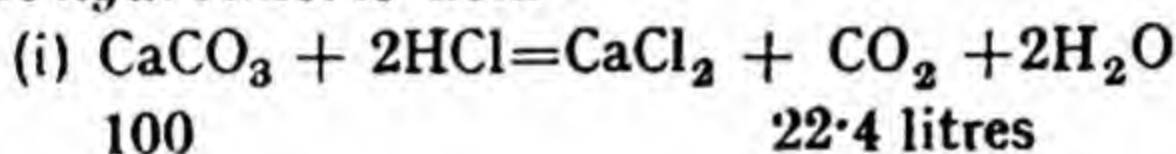
(d) Reaction with oxygen



\therefore 1 vol. of cyanogen will give 2 vols. CO_2 and
1 vol. of nitrogen.

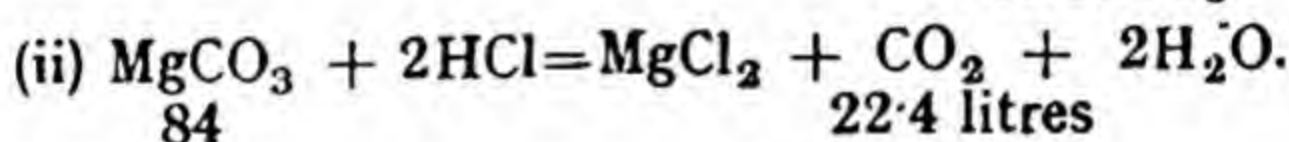
\therefore 1 litre of cyanogen will give 2 litres of CO_2 and
1 litre of nitrogen

7. A sample of dolomite contained 54 % $CaCO_3$, 42 % $MgCO_3$ and 4 % clay. Calculate the volume of CO_2 measured at $10^\circ C$ and 750 mm. pressure which would be evolved on treating 5 gms of the sample with dilute hydrochloric acid.



and 5 gms. of dolomite contains $\frac{5 \times 54}{100} = 2.7$ gms.

of $CaCO_3$



and 5 gms. of dolomite contains $\frac{5 \times 42}{100} = 2.1$ gms.

of $MgCO_3$

From equation (i) 100 gms. of $CaCO_3$ produce 22.4
litres of CO_2 at N. T. P

$$\therefore 2.7 \text{ gms. of } \text{,,} \quad \frac{22.4 \times 2.7}{100}$$

$= 604.8$ m.ls. of CO_2 at N. T. P.

and from equation (ii) 84 gms. of $MgCO_3$ give 22.4 litres
of CO_2 at N. T. P.

$$\therefore 2.1 \text{ gms. of } \text{MgCO}_3 \text{ give } \frac{22.4 \times 2.1}{84}$$

$$= 560 \text{ m ls. of } \text{CO}_2 \text{ at N. T. P.}$$

$$\therefore \text{total vol. of } \text{CO}_2 = 604.8 + 560 = 1164.8 \text{ m.ls. at N. T. P.}$$

$$V = 1164.8 \text{ m.ls.} \quad V_1 = x.$$

$$T = 273 \quad T_1 = 273 + 10 = 283$$

$$P = 760 \quad P_1 = 750$$

$$\therefore \frac{1164.8 \times 760}{273} = \frac{x \times 750}{283}$$

$$\therefore x = \frac{1164.8 \times 760 \times 283}{274 \times 750} = 1202.2 \text{ m.ls.}$$

8. In determining the percentage of ammonia in ammonium sulphate the following results were obtained:-

1.216 gms. of the salt was boiled with excess of caustic soda and the ammonia collected in 100 m.ls. of normal sulphuric acid.

The partly neutralised acid was then titrated with normal caustic soda solution and it required 81.6 m.ls. of this solution to reach the end point. Calculate the percentage of ammonia in ammonium sulphate.

Volume of normal H_2SO_4 taken = 100 m.ls.

Vol. of N. NaOH required for neutralizing the remaining acid = 81.6 m.ls.

\therefore Vol. of N. H_2SO_4 left unused = 81.6 m.ls.

\therefore Vol. of N. H_2SO_4 used for neutralization of ammonia = $100 - 81.6 = 18.4 \text{ m.ls.}$

\therefore Vol. of N. NH_3 obtained = 18.4 m.ls.

Now 1 litre of N. NH_3 contains 17 gms. of ammonia,

$\therefore 18.4 \text{ m.ls. contains } \frac{17 \times 18.4}{100} = 0.3128 \text{ gm. of ammonia.}$

$$\therefore \% \text{age of ammonia} = \frac{0.03128 \times 100}{1.216} = 25.7.$$

9. 20 m ls. of a gaseous hydrocarbon were exploded with 66 m ls. of oxygen. The residual gas after cooling occupied 56 m ls. On treatment with KOH, the volume decreased to 16 m ls. What is the formula of the hydrocarbon?

Vol. of the hydrocarbon = 20 m ls.

Vol. of oxygen used = 66 m ls.

Vol. after cooling = 56 m ls.

Vol. after absorption with KOH = 16 m ls.

\therefore Vol. of CO_2 formed = $56 - 16 = 40$ m ls.

Vol. of oxygen left unused = 16 m ls.

\therefore Vol. of oxygen used = $66 - 16 = 50$ m ls.

Vol. of oxygen used for the formation of 40 m ls. of CO_2 $\left(\begin{array}{ccc} \text{C} & + & \text{O}_2 \\ 1 \text{ vol.} & & 1 \text{ vol.} \end{array} \right) = \text{CO}_2$ } = 40 m ls.

\therefore Vol. of O_2 used for the formation of water } = $50 - 40 = 10$ m ls.

Vol. of water formed from 10 m ls. of oxygen $\left(\begin{array}{ccc} 2\text{H}_2 & + & \text{O}_2 \\ 1 \text{ vol.} & & 2 \text{ vols.} \end{array} \right) = 2\text{H}_2\text{O}$ } = $10 \times 2 = 20$ m ls.

\therefore 20 m ls. of the hydrocarbon give 40 m ls. of CO_2 and 20 m ls. of water.

\therefore 1 Vol. of the hydrocarbon gives 2 vols. of CO_2 and 1 vol. of water

Applying Avogadro's hypothesis,

1 Mol. of the hydro-carbon gives 2 mols. of CO_2 and 1 mol. of H_2O .

\therefore the formula of the hydrocarbon = C_2H_2 .

10. 2 gms. of an acid gave on combustion 0.40 gm. H_2O and 1.95 gm. CO_2 . The acid is dibasic and 0.5 gm. of the silver salt on ignition gives 0.355 gm. silver. Calculate the Empirical and molecular formula of the acid.

(i) Wt. of water formed = 0.040 gm.

∴ amount of Hydrogen present = $\frac{0.040}{9}$ gm.

Wt. of the substance taken = 2 gms.

∴ %age of Hydrogen = $\frac{0.040}{9} \times \frac{100}{2} = 2.22$.

(ii) Wt. of carbon dioxide formed = 0.195 gm.

∴ amount of carbon present = $\frac{0.195 \times 12}{44}$ gms.

∴ %age of carbon = $\frac{0.195 \times 12}{44} \times \frac{100}{2} = 26.6$

(iii) Percentage of oxygen (by difference) = 100

$$-(26.6 + 2.22) \\ = 100 - 28.82 = 71.18.$$

(iv) ∴ C = 26.6 %.

H = 2.22 %.

O = 71.18 %.

Dividing by their respective atomic weights, we get

C = 2.22 1

H = 2.22 1

O = 4.44 2

∴ the Empirical Formula of the acid = CHO_2 .

(v) Wt. of the silver salt = 0.5 gm.

Wt. of silver obtained = 0.355 gm.

∴ Eq. wt. of the silver salt = $\frac{108 \times 5}{355} = 152$.

Hence the Eq. wt. of the acid = $152 - 107 = 45$.

The acid being dibasic, its molecular weight = $45 \times 2 = 90$

(vi) The Empirical formula weight = $12 + 1 + 32 = 45$.
The molecular weight = 90.

$$\therefore \text{The ratio between both} = \frac{90}{45} = 2$$

Hence the molecular formula of the acid = $(\text{CHO}_2)_2$
= $\text{C}_2\text{H}_2\text{O}_4$.

11. 0.571 gm. of a monobasic acid gave on combustion 1.4362 gms. CO_2 and 0.2547 gm. H_2O . 0.2143 gm. of the silver salt gave 0.101 gm. of silver. Calculate the formula of the acid.

(i) Wt. of the acid = 0.571 gm.

Wt. of CO_2 formed = 1.4362.

$$\therefore \text{wt. of carbon present} = \frac{1.4362 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon} = \frac{1.4362 \times 12}{44} \times \frac{100}{0.571} = 68.88.$$

(ii) Wt. of water formed = 0.2547 gm.

$$\text{Wt. of hydrogen present} = \frac{0.2547}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{0.2547}{9} \times \frac{100}{0.571} = 4.9$$

$$\begin{aligned} \text{and } \% \text{age of oxygen (by difference)} &= 100 - (68.88 + 4.9) \\ &= 100 - 73.78 = 26.22. \end{aligned}$$

(iii) C = 68.88%.

H = 4.90%.

O = 26.22%.

Dividing the %ages by the respective atomic weights of the elements, we get

C = 5.74.

H = 4.9.

$$O = 1.64.$$

So that the ratio is 2 : 6 : 7.

∴ The Empirical formula is $C_7H_6O_2$.

(iv) The wt. of the silver salt = 2143 gm.

Wt. of silver obtained = 101 gm.

$$\therefore \text{Eq. wt. of the silver salt} = \frac{108 \times 2143}{101} = 229.$$

$$\therefore \text{The Eq. wt. of the acid} = 229 - 107 = 122.$$

The basicity of the acid = 1.

$$\therefore \text{The molecular weight} = 122.$$

The Empirical formula weight = 122.

$$\therefore \text{The molecular formula} = C_7H_6O_2.$$

12. 0.184 gm. of a substance gave 0.193 gm. of CO_2 and 0.069 gm. of water. 0.2141 gm. gave 0.2410 gm. of silver bromide. Calculate the Empirical formula of the substance.

(i) Wt. of the substance = 0.184 gm.

Wt. of CO_2 formed = 0.193 gm.

$$\therefore \text{Wt. of carbon present} = \frac{0.193 \times 12}{44}.$$

$$\therefore \% \text{age of carbon} = \frac{0.193 \times 12}{44} \times \frac{100}{0.184} = 28.6$$

(ii) Wt. of water formed = 0.069 gm.

$$\therefore \text{Wt. of hydrogen present} = \frac{0.069}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{0.069}{9} \times \frac{100}{0.184} = 4.1$$

(iii) Wt. of the substance = 0.2141 gm.

Wt. of the silver bromide = 0.2410 gm.

$$\therefore \text{wt. of bromine present} = \frac{.2410 \times 80}{188} \text{ gm.}$$

$$\therefore \% \text{age of bromine} = \frac{.2410 \times 80}{188} \times \frac{100}{.241} = 47.8.$$

$$(i v) \text{ Percentage of oxygen (by difference)} = 100 - (28.6 + 4.1 + 47.8) = 100 - 80.5 = 19.5.$$

Dividing by the atomic weights we have the following ratios:—

(v) $\therefore C = 28.6\%$	2.4	4
H = 4.1%	4.1	7
Br = 47.8%	0.59	1
O = 19.5%	1.22	2

\therefore Empirical formula is $C_4H_7BrO_2$.

13. A dibasic organic acid gave the following result:—

0.27 gm. gave 0.054 gm. H_2O and 0.264 gm. CO_2 .

0.32 gm. of the acid neutralised 71.1 m.l.s. of $\frac{N}{10}$ NaOH.

Calculate the molecular formula of the acid.

$$(i) \text{ Wt. of the acid} = .27 \text{ gm.}$$

$$\text{Wt. of } H_2O \text{ formed} = .454 \text{ gm.}$$

$$\therefore \text{wt. of hydrogen present} = \frac{.054}{9} = .006 \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{.006 \times 100}{.27} = 2.22.$$

$$\text{and Wt. of } CO_2 \text{ formed} = .264 \text{ gm.}$$

$$\therefore \text{Amount of carbon present} = \frac{.264 \times 12}{44}$$

$$\therefore \% \text{age of carbon} = \frac{.264 \times 12}{44} \times \frac{100}{.27} = 26.6.$$

and the %age of oxygen (by difference) = $100 - (2.22 + 26.6)$
 $= 100 - 28.82 = 71.18.$

	Dividing by the At. wts.	the ratio
(ii) $\therefore C = 26.6\%$	2.22	1
$H = 2.22\%$	2.22	1
$O = 71.18\%$	4.44	2

\therefore The Empirical formula = CHO_2

(iii) 32 gm. of the acid neutralise 71.1 m.l.s. of $\frac{10}{N}$ NaOH.

\therefore 32 gm. of acid give 71.1 m.l.s. of $\frac{N}{10}$ acid

\therefore 1 litre of the normal acid will be obtained from

$$\frac{32 \times 1000 \times 10}{71.1} = 45 \text{ gms.}$$

\therefore The equivalent wt. of the acid = 45.

Its basicity being 2, the molecular wt. = 90.

\therefore The molecular formula = $\text{C}_2\text{H}_2\text{O}_4$.

14. The analysis of an organic compound containing carbon, hydrogen and oxygen only gave the following results:—
 0.3694 gm. gave 0.8786 gm. CO_2 and 0.4493 gm. water.
 0.169 gm. displaced 53.2 m.l.s. of dry nitrogen at 15°C and 771 mm. pressure in Victor Meyer's apparatus. What is the molecular formula of the substance.

(i) Wt. of the substance = 0.3694 gm.

Wt. of CO_2 formed = 0.8786 gm.

$$\therefore \text{wt. of carbon present} = \frac{0.8786 \times 12}{44}$$

$$\therefore \% \text{age of carbon} = \frac{0.8786 \times 12}{44} \times \frac{100}{0.3694} = 64.9$$

and wt. of H_2O formed = 0.4493 gm.

$$\therefore \text{wt. of hydrogen present} = \frac{.4493}{9}$$

$$\therefore \% \text{age of hydrogen} = \frac{.4493}{9} \times \frac{100}{.3694} = 13.5$$

$$\text{and } \% \text{age of oxygen (by difference)} = 100 - (64.9 + 13.5) \\ = 100 - 78.4 = 21.6.$$

Dividing by At. wts. Ratio of the no. of At.

(ii) C=64.9	5.4	4
H=13.5	13.5	10
O=21.6,	1.35	1

\therefore the Empirical formula = $\text{C}_4\text{H}_{10}\text{O}$.

(iii) Wt. of the substance = 169 gm.

Vol. of air displaced = 53.2 m.ls. at 15°C and 771 mm.

$$\therefore \text{Vol. at N.T.P.} = \frac{53.2 \times 273 \times 771}{288 \times 760} \text{ m.ls.}$$

$$\therefore \text{wt. of hydrogen} = \frac{53.2 \times 273 \times 771}{288 \times 760} \times .00009 \text{ gm.}$$

\therefore V. D. of the compound

$$= \frac{.169 \times 760 \times 288}{53.2 \times 273 \times 771 \times .00009} = 37.$$

$$\therefore \text{Mol. wt.} = 37 \times 2 = 74.$$

The Empirical formula = $\text{C}_4\text{H}_{10}\text{O}$.

$$\therefore \text{Empirical formula wt.} = 48 + 10 + 16 = 74.$$

\therefore The mol. wt = Em. F. wt.

\therefore The molecular formula = $\text{C}_4\text{H}_{10}\text{O}$

15. A liquid containing carbon, hydrogen and oxygen only gave the following result:—

0.3650 gm. gave 0.7318 gm. CO_2 and 0.2984 gm. water. In a Victor Meyer's determination 0.1947 gm. of the liquid

displaced 50.37 m.ls. of air at 13.5°C and 773.2 mm. pressure.
Calculate the molecular formula. (Aq. tension at 13.5°C = 11.5 mm.)

(i) Wt. of the acid = 0.3650 gm.

Wt. of CO_2 formed = 0.7318 gm.

Wt. of carbon present = $\frac{0.7318 \times 12}{44}$ gm.

\therefore %age of carbon = $\frac{0.7318 \times 12}{44} \times \frac{100}{0.3650} = 53$

Wt. of H_2O formed = 0.2984 gm.

\therefore wt. of hydrogen present = $\frac{0.2984}{9}$ gm.

\therefore %age of hydrogen = $\frac{0.2984}{9} \times \frac{100}{0.3650} = 9$.

\therefore %age of oxygen = $100 - (53 + 9) = 100 - 62 = 38$.

Dividing by At. wts. Ratio of no. of atoms.

(ii) C = 53	4.4	2
H = 9	9.0	4
O = 38	2.3	1

\therefore Empirical formula = $\text{C}_2\text{H}_4\text{O}$

(iii) Wt. of the substance = 0.1947 gm.

Vol. of air displaced = 50.37 m.ls. at 13.5°C
[and 773.2 mm.

Aq. tension = 11.5 mm.

\therefore vol. at N.T.P. = $\frac{50.37 \times 273 \times 761.7}{760 \times 286.5}$

\therefore wt. of this vol. of hydrogen =

$\frac{50.37 \times 273 \times 761.7}{760 \times 286.5} \times 0.00009$ gm.

$$\therefore V. D. = \frac{1947 \times 760 \times 286.5}{50.37 \times 273 \times 761.7 \times .00009} = 44.$$

$$\therefore \text{molecular wt.} = 44 \times 2 = 88.$$

$$\text{The Empirical formula wt.} = C_2H_4O = 24 + 4 + 16 = 44.$$

$$\therefore \text{The molecular formula} = C_4H_8O_2.$$

16. *A monobasic acid on combustion gave the following result:—*

0.2699 gm. gave 0.3958 gm. CO₂ and 0.1619 gm. water.

Also it is found that the silver salt contains 54.8 % silver. Calculate the molecular formula.

$$(i) \text{ Wt. of the acid} = 0.2699 \text{ gm.}$$

$$\text{Wt of CO}_2 \text{ formed} = 0.3958 \text{ gm.}$$

$$\text{Wt. of carbon present} = \frac{0.3958 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon} = \frac{0.3958 \times 11}{44} \times \frac{100}{0.2699} = 40\%.$$

$$\text{and wt of H}_2\text{O formed} = 0.1619 \text{ gm.}$$

$$\therefore \text{wt. of hydrogen present} = \frac{0.1619}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{0.1619}{9} \times \frac{100}{0.2699} = 6.66\%$$

$$\text{and \%age of oxygen} = 100 - (6.66 + 40) = 100 - 46.66 = 53.34.$$

%ages • Dividing by At. wt. Ratio of no. of At.

(ii) C = 40%	3.33	1
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H = 6.66%	6.66	2
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O = 53.34%	3.33	1
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$$\therefore \text{Empirical formula} = CH_2O.$$

(iii) The silver salt contains 54.8% silver.

So that 54.8 gms. of silver is present in 100 gms. of the silver salt.

∴ 108 gms. of silver is present in

$$\frac{100 \times 108}{54.8} = 197.$$

∴ eq. wt. of the salt = 197.

and the eq. wt. of the acid = $197 - 107 = 90$.

The acid being monobasic, its molecular wt. also = 90

Now the empirical formula wt. = 30.

$$\therefore \frac{\text{Mol. wt.}}{\text{Emp. F. wt.}} = \frac{90}{30} = 3.$$

Hence the molecular formula = $(\text{CH}_2\text{O})_3 = \text{C}_3\text{H}_6\text{O}_3$.

17. 0.1511 gm. of a substance gave 0.3057 gm. CO_2 and 0.1409 gm. H_2O . By Kjeldahl's method 0.5622 gm. required 6.46 m.l.s. of $\text{N.H}_2\text{SO}_4$ for neutralisation of ammonia. Calculate the molecular formula of the compound.

Wt. of CO_2 formed = 0.3057 gm.

$$\therefore \text{wt. of carbon present} = \frac{0.3057 \times 12}{44} \text{ gm.}$$

$$\therefore \% \text{age of carbon} = \frac{0.3057 \times 12}{44} \times \frac{100}{0.1511} = 55.2$$

and Wt. of H_2O formed = 0.1409 gm.

$$\therefore \text{wt. of hydrogen} = \frac{0.1409}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{0.1409}{9} \times \frac{100}{0.1511} = 10.3.$$

Ammonia

(iii) 0.5622 gm. neutralised 6.46 m.l.s. of $\text{N.H}_2\text{SO}_4$

∴ The amount of ammonia formed = 6.46 m.l.s. of
Normal solution.

Wt. of ammonia in 1 litre of normal solution
= 17 gm.

Wt. of ammonia in 6.46 m.l.s. normal solution

$$= \frac{17 \times 6.46}{1000} = 0.10982 \text{ gm.}$$

∴ 5622 gm. of the substance contain 0.10982 gm.
of ammonia.

∴ %age of nitrogen in the compound =

$$\frac{0.10982 \times 14}{17} \times \frac{100}{5622} = 16.4$$

(iii) %age of oxygen (by difference) = $100 - (55.2 + 10.3 + 16.4) = 100 - 81.9 = 18.1$.

%ages	Dividing by at. wts.	Ratio of no of at.
(iv) C = 55.2	C = 4.6	4
H = 10.3	H = 10.3	9
N = 16.4	N = 1.17	1
O = 18.1	O = 1.13	1

∴ The empirical formula = $\text{C}_4\text{H}_9\text{NO}$

18. 0.3114 gm. of an organic substance gave 0.8061 gm. CO_2 and 0.2230 gm. water and 0.2825 gm. gave 11.53 m.l. of nitrogen collected over water at 15°C and 773 mm. pressure. Find the empirical formula of the compound. (Aq. tension at $15^\circ\text{C} = 12.7 \text{ mm.}$)

(i) Wt. of the substance = 0.3114 gm.

Wt. of CO_2 formed = 0.8061 gm.

Wt. of carbon present = $\frac{0.8061 \times 12}{44} \text{ gm.}$

$$\therefore \% \text{age of carbon} = \frac{.8061 \times 12}{44} \times \frac{100}{.3114} = 70.6.$$

$$\text{Wt. of H}_2\text{O formed} = .2230 \text{ gm.}$$

$$\therefore \text{wt. of hydrogen present} = \frac{.223}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{.223}{9} \times \frac{100}{.3114} = 7.90.$$

(ii) Vol. of nitrogen evolved = 11.53 m.ls. at 15°C and (773-12.7) mm. pressure.

$$\therefore \text{vol. at N.T.P.} = \frac{11.53 \times 273 \times 760.3}{288 \times 760} \text{ m.ls.}$$

$$\therefore \text{wt. of nitrogen formed} =$$

$$\frac{11.53 \times 273 \times 760.3}{288 \times 760} \times .00009 \times 14 \text{ gms.}$$

$$\% \text{age of nitrogen} =$$

$$\frac{11.53 \times 273 \times 760.3}{288 \times 760} \times .00126 \times \frac{100}{.2825} = 4.9.$$

$$\begin{aligned} \text{(iii) \%age of oxygen} &= 100 - (70.6 + 7.9 + 4.9). \\ &= 100 - 83.4 = 16.6. \end{aligned}$$

(iv) %ages. Dividing by at wts. Ratio of no. of a atoms.

C=70.6	5.86	17
H=7.9	7.9	22.6
N=4.9	.35	1
O=16.6	1.04	3

$$\therefore \text{the empirical formula} = \text{C}_{17}\text{H}_{23}\text{NO}_3.$$

19. 0.2965 gm. of an organic substance gave 0.8697 gm. CO_2 and 0.1779 gm. H_2O . 0.1965 gm. gave 22.25 m.ls of nitrogen (dry) at 18°C and 763 mm. pressure. Calculate the empirical formula of the compound.

(i) Wt. of the substance = 0.2965 gm.

Wt. of CO_2 formed = 0.8697 gm.

Wt. of carbon present = $\frac{0.8697 \times 12}{44}$ gm.

\therefore %age of carbon = $\frac{0.8697 \times 12}{44} \times \frac{100}{0.2965} = 80$

(ii) Wt. of H_2O formed = 0.1779 gm.

\therefore Wt. of hydrogen present = $\frac{0.1779}{9}$ gm.

\therefore %age of hydrogen = $\frac{0.1779}{9} \times \frac{100}{0.2965} = 6.68$.

(iii) Wt. of the substance = 0.1965 gm.

Vol. of N_2 evolved = 22.25 m. ls. at 18°C and 763 mm.

\therefore Vol. of N_2 at N.T.P. = $\frac{22.25 \times 273 \times 763}{291 \times 760}$ m.ls.

Wt. of N_2 evolved = $\frac{22.25 \times 273 \times 763 \times 0.00126}{291 \times 760}$ gm.

%age of N_2 = $\frac{22.25 \times 273 \times 763 \times 0.00126}{291 \times 760} \times \frac{100}{0.1965} = 13.32$

As the sum of the %ages is 100 there is no oxygen in the compound.

(iv) %ages.	Dividing by the atomic wts.	Ratio of No. of atom.
C = 80	6.66	7.1 7
H = 6.68	6.68	7.1 7
N = 13.32	0.95	1 1

\therefore the empirical formula = $\text{C}_7\text{H}_7\text{N}$.

20. A substance on analysis gave the following results :-

0.3112 gm. gave 0.4291 gm. CO_2 and 0.0585 gm. H_2O
 0.2293 gm. of the substance gave 0.3969 gm. of a mixture of
 bromide and chloride of silver.

0.2202 gm. of this mixture of the halides was found to
 contain 0.1435 gm. silver. Find the empirical formula of the
 original substance.

(i) Wt. of the substance = 0.3112 gm.

Wt. of CO_2 formed = 0.4291 gm.

Wt. of carbon present = $\frac{0.4291 \times 12}{44}$ gm.

$$\therefore \% \text{age of carbon} = \frac{0.4291 \times 12}{44} \times \frac{100}{0.3112} = 37.9.$$

(ii) Wt. of H_2O formed = 0.0585 gm.

\therefore Wt. of hydrogen present = $\frac{0.0585}{9}$ gm.

$$\therefore \text{percentage of hydrogen} = \frac{0.0585}{9} \times \frac{100}{0.3112} = 2.09.$$

(iii) Wt. of the substance = 0.2293 gm.

Wt. of the mixture formed = 0.3969 gm.

Wt. of the mixture taken = 0.2202 gm.

Wt. of silver present = 0.1435 gm.

Suppose the wt. of silver chloride = x gm.

\therefore wt. of the bromide = (0.2202 - x) gm.

143.5 gm. of AgCl contain 108 gm. of silver.

\therefore x gm. " " $\frac{x \times 108}{143.5}$ gm. of silver

and 188 gms. of AgBr contain 108 gm. of silver.

$$\therefore (\cdot 2202 - x) \text{ gm. AgBr contain } \frac{108 \times (\cdot 2202 - x)}{188} \text{ gm. of silver.}$$

$$\therefore \frac{108 x}{143 \cdot 5} + \frac{108 (\cdot 2202 - x)}{188} = \cdot 1435$$

$$\therefore \cdot 7526 x + \cdot 1265 - \cdot 5744 x = \cdot 1435.$$

$$\therefore \cdot 7526 x - \cdot 5744 x = \cdot 1435 - \cdot 1265.$$

$$\text{Or } \cdot 1782 x = \cdot 0170.$$

$$\text{Or } x = \frac{0170}{\cdot 1782} = \cdot 0955$$

$$\therefore \text{wt. of AgCl} = \cdot 0955 \text{ gm.}$$

$$\text{and wt. of AgBr} = \cdot 2202 - \cdot 0955 = \cdot 1247 \text{ gm.}$$

$$\text{Now } \cdot 2202 \text{ gm. of the mixture contains } \cdot 0955 \text{ gm. of Ag. Cl.}$$

$$\therefore \cdot 3969 \text{ gm. of the mixture contains } = \frac{\cdot 059 \times \cdot 3969}{\cdot 2202} = \cdot 1721 \text{ gm. of AgCl}$$

$$\therefore \text{wt. of AgBr} = \cdot 3969 - \cdot 1721 = \cdot 2248 \text{ gm. of AgBr.}$$

$$\begin{aligned} \text{Now wt. of chlorine in } \cdot 1721 \text{ gm. of AgCl} \\ = \frac{\cdot 1721 \times 35 \cdot 5}{143 \cdot 5} = \cdot 0426 \text{ gm.} \end{aligned}$$

$$\therefore \text{percentage of chlorine} = \frac{\cdot 0426 \times 100}{\cdot 2293} = 18 \cdot 9$$

$$\begin{aligned} \text{and wt. of bromine in } \cdot 2248 \text{ gm. of AgBr} &= \frac{\cdot 2248 \times 80}{188} \\ &= \cdot 0956 \text{ gm.} \end{aligned}$$

$$\therefore \text{percentage of bromine} = \frac{\cdot 0956 \times 100}{\cdot 2293} = 41 \cdot 6.$$

(iv) Percentages	Dividing by At. wts.	Ratio of No. of atoms.
C=37.9	3.16	6
H=2.09	2.09	4
Cl=18.9	0.53	1
Br=41.6	0.52	1

\therefore the empirical formula = C_6H_4ClBr .

21. An organic compound containing sulphur gave on analysis the following results. 0.1348 gm. gave 0.322 gm. CO_2 and 0.662 gm. H_2O . 0.1564 gm. gave 0.774 gm. barium sulphate. Calculate the empirical formula of the compound.

- (i) Wt. of the substance = 0.1348 gm.
Wt. of CO_2 formed = 0.322 gm.

$$\therefore \text{wt. of carbon present} = \frac{0.322 \times 12}{44} \text{ gm.}$$

$$\therefore \text{percentage of carbon} = \frac{0.322 \times 12}{44} \times \frac{100}{0.1348} = 65.1.$$

- (ii) Wt. of H_2O formed = 0.662 gm.

$$\text{Wt. of hydrogen present} = \frac{0.662}{9} \text{ gm.}$$

$$\therefore \% \text{age of hydrogen} = \frac{0.662}{9} \times \frac{100}{0.1348} = 5.4$$

- (iii) Wt. of the substance = 0.1564 gm.

$$\text{Wt. of } BaSO_4 \text{ formed} = 0.774 \text{ gm.}$$

$$\therefore \text{wt. of sulphur present} =$$

$$\frac{0.774 \times 32}{233} \quad (\because 233 \text{ gms. of } BaSO_4 \text{ contain 32 gms. of sulphur})$$

$$\therefore \% \text{age of sulphur} = \frac{0.774 \times 32}{233} \times \frac{100}{0.1564} = 7.9$$

$$\text{(iv) \%age of oxygen (by difference)} = 100 - (65.1 + 5.4 + 7.9) \\ = 100 - 78.4 = 21.6$$

(v) %ages.	Dividing by At. wts.	Ratio of No. atoms.
C=65.1	5.4	26
H=5.4	5.4	26
S=7.9	0.21	1
O=21.6	1.42	7

\therefore the empirical formula = $\text{C}_{26}\text{H}_{26}\text{SO}_7$.

22. An organic liquid gave the following results on analysis.

$$\text{C} = 10.06\%, \text{H} = 0.84\%, \text{Cl} = 89.1\%.$$

Its vapour density was found to be 60. Calculate the molecular formula of the substance.

(i) %age Composition	Dividing by At. wts.	Ratio of No. of atoms.
C=10.06	.84	1
H=0.84	.84	1
Cl=89.1	2.51	3

\therefore the empirical formula = CHCl_3

(ii) the vapour density = 60.

$$\therefore \text{the mol. wt.} = 60 \times 2 = 120.$$

$$\text{The empirical formula wt.} = 12 + 1 + 106.5 = 119.5.$$

\therefore the molecular formula is the same as the empirical formula = CHCl_3

23. 0.27 gm. of an organic compound gave on combustion 0.264 gm. of CO_2 and 0.162 gm. of water. 0.14 gm. of the substance was Kjeldahlised and NH_3 liberated was passed through 50 m.l.s. of $\frac{N}{10} \text{H}_2\text{SO}_4$. Excess of the acid required

9.5 m.l.s. of $\frac{N}{5}$ KOH solution. The compound is a derivative of formic acid. What is its formula if its mole. wt. be 45 ?

$$\text{Percentage of carbon} = \frac{.264 \times 12}{44} \times \frac{100}{.27} = 26.66\%$$

$$\text{Percentage of hydrogen} = \frac{.162 \times 2}{18} \times \frac{100}{.27} = 6.66\%$$

Excess of the acid required 9.5 m.l.s. of $\frac{N}{5}$ KOH

Or 19 m.l.s. of $\frac{N}{10}$ KOH

\therefore acid used for ammonia

$$= 50 - 19 = 31 \text{ m.l.s. of } \frac{N}{10} \text{H}_2\text{SO}_4$$

\therefore 31 m.l.s. of $\frac{N}{10}$ ammonia were produced.

Now 1000 m.l.s. of normal ammonia contain

14 gms. of nitrogen

$$\therefore 31 \text{ m.l.s. of } \frac{N}{10} \text{ ammonia will contain } \frac{31 \times 14}{1000} \times \frac{1}{10}$$

$$\therefore \text{percentage of nitrogen} = \frac{31 \times 14}{1000 \times 10} \times \frac{100}{.14} = 31\%$$

$$\text{Percentage of oxygen} = 100 - [26.66 + 6.66 + 31] = 35.68.$$

Dividing the percentages by atomic weights,

$$\text{C} = \frac{26.66}{12} = 2.22$$

$$\text{H} = \frac{6.66}{1} = 6.66$$

$$N = \frac{31}{14} = 2.22$$

$$O = \frac{35.68}{16} = 2.23$$

The numbers are in the ratio 1 : 3 : 1 : 1

∴ Emp. formula of the compound is CH_3NO

Empirical formula weight = $12 + 3 + 14 + 16 = 45$

Mole. wt. = 45

∴ Molecular formula is also CH_3NO .

Now as the compound is a derivation of formic acid, H COOH , its formula is HCONH_2 .

24. 0.10 gm. of an organic substance gave on combustion 0.147 gm. CO_2 and 0.06 gm. H_2O . When heated with soda lime it gave a hydrocarbon which contained 75% carbon. Deduce the structural formula of the organic acid.

$$\text{Percentage of carbon} = \frac{.147 \times 12}{44} \times \frac{100}{.10} = 40.1\%$$

$$\text{Percentage of hydrogen} = \frac{.06 \times 2}{18} \times \frac{100}{.10} = 6.66\%$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100 - [40.1 + 6.66] \\ &= 100 - 46.76 = 53.24\% \end{aligned}$$

Dividing the percentage of each element by its atomic weight we get atomic ratio,

$$C = \frac{40.1}{12} = 3.34$$

$$H = \frac{6.66}{1} = 6.66$$

$$O = \frac{53.24}{16} = 3.33$$

These numbers are in the ratio 1 : 2 : 1

∴ Emp. formula is CH_2O .

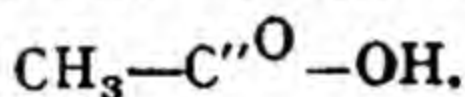
On treatment with Soda lime it gives a hydrocarbon, ∴ it must be an acid.

In the hydrocarbon the ratio of carbon to hydrogen is as 75 : 25 or 3 : 1

3 gms. carbon combine with 1 gm. hydrogen

∴ 12 " " " " 4 " "

Or one atom of carbon combines with 4 atoms of hydrogen. i. e. the hydrocarbon is CH_4 . This is obtained from acetic acid, CH_3COOH . or $\text{C}_2\text{H}_4\text{O}_2$ which is double the Empirical formula. Therefore the given substance is acetic acid and its structural formula is



25. An organic compound gave the following results on analysis 0.146 gm. of it yielded on combustion 0.264 gm. of CO_2 , 0.126 gm. of water and 22.4 m.l.s. of N_2 at N. T. P.

On treatment with Bromine water and caustic potash it gave ethyl amine. What is the structural formula of the compound.

$$\text{Percentage of carbon} = \frac{0.264 \times 12}{44} \times \frac{100}{0.146} = 49.3\%$$

$$\text{Percentage of hydrogen} = \frac{0.126 \times 2}{18} \times \frac{100}{0.146} = 9.6\%$$

$$\text{Wt. of 22.4 m.l.s. of nitrogen N.T.P} = \frac{28}{1000} \text{ gm.}$$

[as 22.4 litres weigh 28 gms.]

$$\therefore \text{percentage of nitrogen} = \frac{28}{1000} \times \frac{100}{0.146} = 19.2\%$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100 - (49.3 + 9.6 + 19.2) \\ &= 100 - 78.1 = 21.9\% \end{aligned}$$

Dividing the percentage of each element by its atomic weight we get the atomic ratio.

$$C = \frac{49.3}{12} = 4.11$$

$$H = \frac{9.6}{1} = 9.6$$

$$N = \frac{19.2}{14} = 1.37$$

$$O = \frac{21.9}{16} = 1.37$$

These numbers are in the ratio 3 : 7 : 1 : 1

∴ Emp. formula = C_3H_7NO

By the action of Br_2 and KOH we get ethyl amine.

∴ the compound must be propionamide $CH_3CH_2CONH_2$

CHAPTER XVII

MISCELLANEAUS PROBLEMS

1. Find the empirical formula of a substance having the following percentage composition:—

Oxygen=38.1, Hydrogen=0.8, Phosphorous=24.6, Sodium=36.5.

2. 0.4 gm. of pure calcium carbonate was found to require 45 m.l.s. of dilute Hydrochloric acid for complete neutralisation. Calculate the normality of the acid?

3. The chloride of a trivalent element contains 40.5% of chlorine. Find its atomic weight?

4. 0.2 gm. of anhydrous dibasic acid gave on combustion 0.4 gm. water and 1.95 gm. carbon dioxide. 0.5 gm. of its silver salt left on ignition 0.355 gm. silver. What is the molecular formula of the acid?

5. When 20 m.l.s. of sulphuric acid are precipitated by a Barium salt. 1.224 gms. of Barium sulphate are formed. Calculate the normality of the acid?

(P.U. 1940)

6. 2.83 gms. of a gas occupy 3.85 litres at 20°C and 780 mm. pressure. Find the molecular weight of the gas?

7. 22.0 m.l.s. of moist air was collected at 16.5°C and 707.5 mm. pressure when 0.1008 of a substance was vapourised in Victor Meyer's apparatus. Determine the molecular weight of the substance?

[Aq. Tens. at 16.5° = 13.5 mm.]

(P.U. 1943)

8. 2.033 gm. of a compound gave 3.780 gm. carbon dioxide and 0.1288 gm. water on combustion. 0.1877 gm. of the same compound generated 31.7 m.l.s. of nitrogen at 14°C and 758 mm. pressure. Calculate its empirical formula?

(P.U. 1922, 25, 39)

9. Ammonia generated by decomposition of 1.525 gm. of a substance by Kjeldahl's method, was passed into 30 m.l.s. of normal HCl. The unreacted acid required 120 m.l.s. of decinormal caustic soda for mentalisation. Find the percentage of nitrogen in the compound.

(P.U. 1938)

10. How many m.l.s. of N/10 caustic soda solution would be required to neutralise 0.244 gm. of benzoic acid?

11. 0.1475 gm. of a nitrogeous substance was distilled into 50 m.l.s. of $\frac{\text{N}}{10}$ HCl and the excess of the acid required 25 m.l.s. of $\frac{\text{N}}{10}$ alkali for exact neutralisation. What is the percentage of nitrogen in the compound?

(P. U. 1933)

12. 0.2457 gm. of a volatile substance displaced in Victor Meyer's apparatus 30 m.l.s. of air over water at 17°C and 774.5 mm. pressure. What is the molecular weight of the substance?

Aq. tens. at 17°C = 14.5 mm.)

13. A substance gave the following percentages:—
C = 54.5, H = 9.09 and oxygen by difference, 0.1 gm. of the substance displaced in Victor Meyer's apparatus 27 m.l.s. of air at 15°C and 745 mm. pressure. Determine the molecular formula of it.

(Aq. tens. at 15°C = 12.7 mm.)

(P. U. 1937)

14. The density of oxygen is 16 and of nitrogen 14 at 0°C and 760 mm. pressure. At what temperature Oxygen will have the same density as of nitrogen at 0°C . at normal pressure ?

15. In a Victor Meyer's apparatus 0.1104 gm. of chloroform displaced 23.2 m.l.s. of air at 19°C and 772 mm. pressure. Calculate its vapour density.

(Aq. tens. at $19^{\circ}\text{C}=15.4$) & (1 m.l. weighs .00009 gm.)

16. On combustion 0.45 gm. of a dibasic organic acid gave .44 gm. of carbon dioxide and .09 gm. of water. 0.76 gm. of its silver salt left on ignition .54 gm. of silver. What is the acid ?

17. It was found on analysis the black oxide of copper the red oxide of copper, litharge, red lead and lead peroxide contain 79.9, 88.3, 92.3, 90.6 and 86.6 percent of metal respectively. Establish the Law of multiple proportion from the data.

18. 0.2 gm. of a compound containing C, H, N & O, on combustion gave 74.6 m.l.s. of nitrogen gas at N. T. P. & .147 gm. CO_2 & .12 gm. water. Find the simplest formula of the compound ?

(P. U. 1941)

19. 2.3 gm. of a substance was Kjeldahlised and ammonia passed into 60 m.l.s. of normal HCl solution. The excess of acid was neutralised by 36.8 m.l.s. of normal caustic soda. Calculate the percentage of nitrogen ?

20. The chloride of an element has vapour density 59.25 and the oxide of the same element contains 33.3% of the element.

Calculate Valency, Equivalent and Atomic weights of the element.

(P. U. 1941)

21. 1.5 gms. of pure carbonate of a divalent metal produce on heating .855 gm. of its oxide. Calculate the atomic weight of the metal :

(P. U. 1942)

22. What will be the net annual profit of running a sulphuric acid factory of which the daily out put amounts to 20 mds. of the commercial acid. The pure sulphur used in the preparation costs Rs. 7/- per md. and the commercial acid produced (70% H_2SO_4) sells at 4 annas per seer. The other expenses which the factory has to bear are the establishment charges amounting to Rs. 500/- per mensem, the interest on the outlay amounting to Rs. 4000/- per annum and the depreciation and repair charges amount to Rs. 10000 per annum.

(P. U. 1933)

23. A compound containing C, H and O only gave the following results on analysis :—

0.146 gm. gave 0.374 gm. CO_2 and 0.154 gm. H_2O . Its vapour density was found to be 43. The compound reacts with NH_2OH and $\text{C}_6\text{H}_5\text{NH} \cdot \text{NH}_2$ but not with CH_3COCl . On oxidation it gives a mixture of acetic acid and other acids. What is the compound.

24. 0.5 gm. of an organic compound containing C, H and Cl only gave on combustion 0.0378 gm. of H_2O and 0.1844 gm. of CO_2 . By Victor Meyer's method 0.292 gm of this substance displaced 59.53 m.ls. of air at 22°C and 755 mm. pressure. This substance gave an obnoxious odour on treatment with aniline and alcoholic potash. What is the structural formula of the compound?

25. An organic substance has $\text{C}=58.5\%$; $\text{H}=7.3\%$, $\text{N}=34.2\%$. Its V. D. is 20.5. On reduction it gives a substance containing $\text{C}=53.3\%$. The reduced product reacts with HNO_2 to give N_2 . Assign a structural formula to the substance.

26. A sample of coal gas was found to contain 40% hydrogen, 35% methane, 15% carbon monoxide, and 10% acetylene. 100 volumes of this gas were mixed with 600 volumes of air (containing 21% oxygen) in a eudiometer tube and exploded. Calculate the volume and composition of the resulting mixture on cooling.

(E.P.U. 1949)

27. 1.20 gms. of a commercial sample of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$ were dissolved in 200 m.l.s. of water. 10 m.l.s. of this solution required 8.5 m.l.s. of decinormal potassium permanganate solution for complete oxidation. Calculate the percentage purity of the sample.

(E.P.U. 1949)

28. 0.1 gm. of a volatile substance, on vapourization in Victor Meyer's apparatus, displaced 27 m.l.s. of moist air measured at $15^\circ C$. and 740 mm. pressure. Calculate the molecular weight of the substance.

(E.P.U. 1949)

ANSWERS

CHAPTER I

- | | | | |
|---|--------------|---|-------------------|
| 1 | 29940 | 5 | 35.34 c. ft. |
| 2 | 736.5mm. | 6 | 148000000 kilo m. |
| 3 | 61.03, 28.31 | 7 | 299300 |
| 4 | 2779 gms. | | |

CHAPTER II

- | | | | |
|---|---------------------------|----|-----------------------------|
| 1 | 27.17 m.ls. | 8 | 68.75% water, 31.25% milk |
| 2 | 10.91 | 9 | $O_2 = 50\%$, $O_3 = 50\%$ |
| 3 | 1.44 gms. per litre. | 10 | 2.22 |
| 4 | 1.5. | 11 | .64 |
| 5 | 16.1 m.ls. | 12 | 25 m.ls. |
| 6 | .9858 | | |
| 7 | Water : alcohol : 40 : 60 | | |

CHAPTER III

- | | | | |
|---|---------------------------|----|-------------|
| 1 | 486.8 | 9 | 22.31 |
| 2 | 98.7 m.ls., 104.1 m.ls. | 10 | 14.01 |
| 3 | 153.1 m.ls., 258.14 m.ls. | 11 | 24.6 |
| 4 | 147°C | 12 | 146.34 m.ls |
| 5 | [a] 21.04 m.ls. | 13 | 181.3 mm. |
| | [b] 43.75 m.ls. | 14 | 8531 mm. |
| | [c] 91.2 m.ls. | 15 | 9.81 litres |
| 6 | [a] 42 m.ls. | 16 | 16.77 m.ls. |
| | [b] 206.05 m.ls. | 17 | 69.90 m.ls. |
| 7 | 400 mm. | 18 | 124.2 Sec. |
| 8 | -23°C | 19 | 0.9727 |

- 20 2.83 m.ls.
- 21 O_3
- 22 45.64 m.ls.
- 23 71.55 m.ls.
- 24 50.39
- 25 24.63
- 26 25.37
- 27 39.91
- 28 7.59 m.ls.
- 29 16
- 30 279.05 m.ls.

- 31 29.56
- 32 25.19
- 33 $39^\circ C$
- 34 524.3 m.ls.
- 35 364.6 m.ls.
- 36 2.549 litres
- 37 [a] 98.40 m.ls.
[b] 100.5 m.ls.
- 38 47.01 cm.
- 39 63.16 m.ls.

CHAPTER IV

- 1 $Cl=1, Ag=3.05$
- 3 1:2
- 4 1:2:3:4
- 5 3:5

- 6 3:6:4
- 16 $C=42.46\%$
 $O=57.54\%$
- 23 M_2O_3

CHAPTER V

- 1 32.24
- 2 9.475
- 3 11.5
- 4 28.5
- 5 18.7
- 6 32.5
- 7 29.4
- 8 31.5
- 9 109.3
- 10 35.5
- 11 80
- 12 10.3

- 13 .8559 gm; 2.916; 7911 gm.
- 14 29.4
- 15 .594
- 16 20
- 17 21.16
- 18 $\begin{cases} O=8.06 \\ C_4=31.5 \end{cases}$
- 19 12.09
- 20 16.128
- 21 31.49
- 22 9.25

23 32.97

24 32.10

25 32.75

26 $\begin{cases} 18.62 \\ 27.89 \end{cases}$

27 32.83; 33.91

28 39.05

29 31.5

30 31.77

CHAPTER VI

1 133.7

2 189

3 38.7

4 50.28

5 279.05 Sec.

6 40.32

7 25.37

8 39.91

9 V.D=61.2, M.W=122.4

10 88,

11 120.14

12 17.02

13 0.3336 gm.

14 119.1

15 102.7

16 41.16

17 75.88

18 78

19 38.06, 72.12

20 118.1

21 85.40

CHAPTER VII

1 14

2 12

3 16

4 27

5 113.4, 203, 56

6 99.9, 199.98, 203.4

7 24.09

8 24.03

9 35.45

10 59

11 5.2

12 226.2

13 31

14 194.4

15 69.95

16 65

17 (a) 59.7

(b) 19.9

(c) 3

18 118.6

19 27, 9, 3

20 59

21	27	27	194.4
22	26.985	28	25, 75, 3
23	26.958	29	63.52
24	107.6	30	24.28
25	9.018; 27.054	31	18.67, 56.01, 3.
26	(a) 27.066	32	27
	(b) 3	33	87.42

CHAPTER VIII

- 1 (a) $\begin{cases} K=31.8 \\ O=39.2 \\ Cl=29 \end{cases}$ (d) 30
 (b) $Fe=70, O=30$ (e) 22.23
 (c) $Cu=25.6, S=12.8,$ (f) 47.06
 $O=25.6, H_2O=36.04$ 3 $Na_2O=21.7, CO_2=15.4$
 (d) $H=1.6, N=22.23,$ $H_2O=63$
 $O=76.17$ 4 16.47, 13.86
 (e) $Mg=9.76, S=13.01$ 5 [a] $Ca=40, C=12,$
 $O=26.01, H_2O=$ $O=48$
 51.22 [b] $Fe=14.286_4$
 (f) $Fe=20.14, S=11.51$ $S=16.32, H=2.041$
 $O=23.02, H_2O=$ $O=32.71, N=7.144$
 45.32 $H_2O=27.55$
 (g) $Al=52.94, O=47.06$ [c] $Zn=22.65, S=11.15$
 (h) $K=35.56, Fe=17.02$ $O=22.30, H_2O=43.9$
 $C=21.88, N=25.53$ [d] $Pb=62.6, N=8.4,$
 $O=29$
 2 (a) 42.11 [e] $Mg=11.96, Cl=34.87$
 (b) 38.10 $H_2O=53.16$
 (c) 53.33 [f] $K=14.04, Al=9.72$
 $Si=30.24, O=46$

[g] Na=29·11, S=40·50		H ₂ O=14·75
O=30·38	6	36·07
[h] Ba=56·14,	7	62·94
Cl=29·10,		

CHAPTER IX

1 [a] H ₄ P ₂ O ₇	MgCl ₂ , 6H ₂ O
[b] HNO ₃	3 K AlSi ₃ O ₈
[c] Al ₂ O ₃	4 Al ₂ O ₃ , 2 SiO ₂ , 2H ₂ O
[d] KHSO ₄	5 AS ₄ O ₆
[e] K ₂ Cr ₂ O ₇	6 Sn ₂ Cl ₄
[f] Na ₂ S ₂ O ₃	7 Na ₂ HPO ₃
2 MgSO ₄ , 7H ₂ O,	8 Na ₂ S ₂ O ₃
FeSO ₄ , 7H ₂ O,	9 Na ₂ SO ₄ , 10H ₂ O
BaCl ₂ , 2H ₂ O,	10 Mg NH ₄ PO ₄ , 6H ₂ O
ZnSO ₄ , 7H ₂ O,	MnCl ₂ ; Na ₂ HPO ₄ ,
CuSO ₄ , 5H ₂ O,	K ₃ Fe(CN) ₆

CHAPTER X

1 21·25 gms. and 5·6 litres	CO ₂ =22 gms.
2 2·4747 litres	9 1·68 litres
3 ·451 gm. HCl	10 10 m.ls.
4 { Lime=3·949 gms.	11 6·28 litres
NH ₃ =1·905 gms.	12 ·569% impurity
CaCl ₂ =6·225 gms.	13 2·42 litres
H ₂ O=2·019 gms.	14 5952·3 cubic ft. air
5 226	15 Oxygen=23·25 litres
6 19·33 gms.	CO ₂ =7·75 litres
7 47 gms.	SO ₂ =15·5 litres
8 Hcl=182·5 gms.,	16 65%

- | | | | |
|----|---|----|---|
| 17 | $\text{Zn} = 7.1 \text{ gms.}$ | 26 | 1.218 litres |
| | $\text{H}_2\text{SO}_4 = 10.5 \text{ gms.}$ | 27 | 42.39 gms. |
| 18 | 300 m.ls. | 28 | $\text{S} = 2.413; \text{SO}_2 = 1.43 \text{ gms.}$ |
| 19 | 519.5, 530.4 | | water = .803 gm. |
| 20 | $\text{HCl} = 158 \text{ gms.}$ | 29 | 29.57 |
| | $\text{MnO}_2 = 31.06 \text{ gms.}$ | 30 | 0.2 litres |
| 21 | 23.3 gms. | 31 | $\text{MgCO}_3 = 45.65$ |
| 22 | H_2S | | $\text{CaCO}_3 = 54.35$ |
| 23 | $\text{O}_2 = 500 \text{ m.ls.}$ | 32 | 42 per cent |
| | $\text{CO}_2 = 400 \text{ m.ls.}$ | 33 | 98, 136 |
| 24 | 82.5% | 34 | $\text{NaCl} = 42.69; \text{KCl} = 57.31$ |
| 25 | 28.25 gms. | 35 | 6.0297 gms. |

CHAPTER XI

- | | | | |
|----|------------|----|---------------------------|
| 1 | 14.7 m ls. | 18 | .157 N; .75 gm. per litre |
| 2 | .8 gm. | 19 | 490.2 m.ls. |
| 3 | 83.3 % | 20 | 77.318 % |
| 4 | 16.7 % | 21 | 43.36 % |
| 5 | 42.44 % | 22 | 90 % |
| 6 | 22.4 gms. | 23 | 306.85 m.ls. |
| 8 | 13.6 % | 23 | 10 m.ls. |
| 10 | 715 m.ls. | 25 | 46.73 m.ls. |
| 11 | .464 N | 26 | 43.53 % |
| 12 | .2126 N | 27 | 3.779 gms. |
| 13 | 23.72 % | 28 | 32.43 |
| 15 | 90 % | 29 | 0.325 N alkaline |
| 16 | Dibasic | 30 | 50 |
| 17 | 50 m.ls. | | |

CHAPTER XII

1	C=53.5; H=15.5	12	13.36 %
	O=31.4	13	13.33
2	C=26.60; H=2.22;	14	65.5
	O=71.18	15	12.39
3	C=26.666; H=2.222;	16	14.05
	O=71.112	17	49.01
4	16.67 %	18	16.53 %
5	19.71 %	19	14.12
6	54.61 %	20	23.72
7	C=39.9; H=6.7	21	C=29.27; H=5.69; Br
	O=53.4		=65.49
8	C=60, H=5, N=35	22	C=52.64, H=28.72;
9	C=40.6; H=8.5;		N=14.95, O=3.69
	N=23.7; O=27.2	23	16.68
10	39.86	24	10.3
11	31.56	25	15.51 %

CHAPTER XIII

1	$C_8H_5NO_2$	11	$C_8H_5NO_2$
2	$C_2H_4O_2$	12	C_3H_7Br
3	$C_4H_8O_2$	13	C_6H_7N
4	C_2H_5OH	14	$C_2H_5NH_2$
5	$C_6H_8N_2$	15	$C_4H_{11}N$
6	C_3H_7Br	16	$C_7H_9NO_2$
7	C_6H_7N	17	$C_2H_7NO_2$
8	C_3H_6O	18	$C_4H_8O_2$
9	C_6H_5COOH	19	CH_4N_2O
10	CH_2O	20	$C_{14}H_{10}SO$

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